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METAL VALUE RECOVERY
FROM
METAL HYDROXIDE SLUDGES

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A two-year study investigating the potential for metal value recovery from metal hydroxide sludges has been completed. The objectives of the study were to:

- Develop a flowsheet to separate and recover metal values from metal finishing hydroxide sludge materials and operate on a laboratory scale (Phase I),
- Develop a test assembly of unit operations to accomplish the separation of metal values on a pilot scale of 75-100 pounds of sludge per day,
- Verify that the pilot scale unit operations accomplish appropriate separations, and
- Delineate potential operational problems.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the application of commercially developed hydrometallurgical processes to the recovery of metal values from complex metal finishing hydroxide sludges. Information in this report will be useful to the electroplating and waste disposal industries in general and to other industries responsible for treatment and disposal of metal bearing process solutions.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

METAL VALUE RECOVERY
FROM
METAL HYDROXIDE SLUDGES

ABSTRACT

A two year study investigating the potential for metal value recovery from metal hydroxide sludges has been completed. The objectives of the study were:

- Develop a flowsheet to separate and recover metal values from metal finishing hydroxide sludge materials,
- Develop a test assembly of unit operations to accomplish the separation of metal values on a scale of 75-100 pounds of sludge per day,
- Verify that the large scale unit operations accomplish appropriate separations and,
- Delineate potential operational problems.

The results of the first phase research successfully accomplished the required objectives. Flowsheets were designed and tested on a laboratory scale prior to full-scale testing. The flowsheets consist of: sulfuric acid leaching; iron removal by jarosite precipitation (high iron bearing solutions) or iron solvent extraction (low iron bearing solutions); copper removal by solvent extraction and copper recovery by either electrowinning or copper sulfate crystallization; zinc removal by solvent extraction and zinc recovery as zinc sulfate by crystallization; chromium oxidation and subsequent recovery by lead chromate precipitation; nickel removal by sulfide precipitation or nickel sulfate crystallization; final solution clean-up of low concentration residual ions by ion exchange.

Full scale tests have been performed to ascertain the applicability of each unit operation. Continuous tests have been performed to investigate

solvent reagent degradation; to develop mass balances; and to delineate operational problems. The successful application of metallurgical unit operations to multi-component complex mixed metal sludges has demonstrated that treatment of such material is possible and economical.

This report was submitted in fulfullment of Grant NumberCR-809305-10 by Montana Tech Foundation and Grant NumberCR-810736-01 by Montana College of Mineral Science and Technology under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period: July 1, 1982 to September 30, 1983 for Grant NumberCR-809305-01 and from July 1, 1983 to September 30, 1984 for Grant NumberCR-810736-01.

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LIST OF ABBREVIATIONS, SYMBOLS AND DEFINITIONS

Abbreviations	
IX	Ion Exchange
SP	Selective Precipitation
SX	Solvent Extraction
AA	Atomic Absorption
D_2EHPA^-	Di-2-ethylhexyl phosphoric acid
DNNSA	Dinonylnapthalene Sulfonic Acid
ICP	Induction Coupled Plasma Spectrophotometry
KERMAC 470B	Solvent Extraction Diluent
KERMAC 510	Low Aromatic Solvent Extraction Diluent
LIX-622	Henkel Reagent: Composition Unreported
LIX-64N	Henkel Reagent: 2-Hydroxy-5-nonylbenzophenone oxime with 5,8-Diethyl-7-hydroxy-6-dodecanone oxime
P5100	ACORGA Reagent: Substituted salicyl aldoxime and nonyl phenol
EHO	Ethyl hexyl oxime
v/o	Volume Percent
w/o	Weight Percent
FCC	Factored Capital Cost
FCAC	Factored Capital Annual Cost

Definitions	
Crud	A stable phase mixture that forms during solvent extraction at the aqueous-organic interface that does not break up regardless of separation times.
Muck	An unstable phase mixture that forms during solvent extraction at the aqueous-organic interface that breaks up if sufficient separation times are allowed.

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SECTION 1

INTRODUCTION

1.1. PROBLEM DEFINITION

In recent years increased emphasis has been placed on preventing the introduction of heavy metal containing industrial wastewaters into publicly owned treatment works and the environment. Legislation has established regulatory authority for controlling the discharge of heavy metals into the environment. It also has mandated resource recovery whenever economically feasible. Many treatment and control technologies have come into existence to remove metals from these wastewater, i.e., a sludge, concentrate, or regenerate form is created and is, in most cases, disposed of in a landfill. Metals are recoverable, but are not recovered significantly because of a lack of proven technologies.

Process wastewaters from the metal finishing and electroplating industry contain cyanides and heavy metals. These wastewaters have a detrimental effect on the environment if discharged directly. Such discharges are regulated by Federal, State, County or City ordinances, and require installation of treatment technology. One of the treatment technologies presently in use is oxidation (or reduction), neutralization and precipitation, which destroys cyanide and removes heavy metals as a hydroxide sludge. This product has traditionally been disposed in hazardous landfill sites.

Disposal in landfills has certain inherent disadvantages:

1. Perpetual maintenance of the disposal site is required,
2. Dilution in metal content by mixing with other types of waste materials and,

3. Permanent loss of non-renewable metals.

If heavy metals are recovered from metal finishing sludges, it will alleviate or reduce the disposal problem and provide for conservation of energy and metal resources. The present study outlines a technical methodology to treat metal bearing sludges by hydrometallurgical techniques.

The treatment of hydroxide sludges for metal value recovery will produce several beneficial results, i.e., economic benefits from the metal values recovered will help offset the cost of recovery/treatment; non-renewable resource metals will be recycled for use by society; and there will be significantly less hazardous material to be disposed of in landfills.

1.2. PURPOSE AND OBJECTIVES

The purpose of the present study was to investigate at an advanced laboratory scale the potential for application of well established hydrometallurgical techniques to a mixed metal sludge. The design, development, fabrication, acquisition, assembly and testwork for such a treatment system has been conducted at the Montana Tech Foundation Mineral Research Center in Butte, Montana (Phase I). Further testwork (Phase II) has been conducted at Montana College of Mineral Science and Technology, Butte, Montana, and at a waste generating site in Camarillo, California.

The objectives of the study included:

- Develop a flowsheet to separate and recover metal values from metal finishing hydroxide sludge materials,
- Develop a test assembly of unit operations to accomplish the separation of metal values on a scale of 75-100 pounds of sludge per day, and
- Verify that the large scale unit operations accomplish appropriate separations and establish the metal recovery efficiency for each unit operation; delineate process and materials handling problems when treating complex mixed metal sludge materials.

1.3. STUDY METHODOLOGY

The experimental study was conducted in two phases. The first phase study objectives were to develop preliminary flowsheets for the separation and recovery of metal values from mixed metal sludge materials; to perform laboratory studies to test the applicability of the preliminary flowsheets; to develop a test assembly of unit operations capable of treating 75-100 pounds of sludge per day, and to conduct preliminary testwork in the test assembly to delineate conditions for successful operation and/or to note potential operational problems.

Phase I of the study was conducted by the Montana Tech Foundation, a not for profit organization, at its Minerals Research Center in Butte, Montana. The technical supervision of the project was performed by Dr. L. G. Twidwell, Montana Enviromet.

A team of extractive metallurgists was assembled as an advisory and review group to propose, discuss and select potential flowsheets for laboratory testing and development. The team included: Dr. L. G. Twidwell, Director of Montana Enviromet and Professor of Metallurgical Engineering at the Montana College of Mineral Science and Technology, whose expertise is pyrometallurgy and hydrometallurgy; Dr. D. Robinson, consultant for DREMCO Corporation, whose expertise is electrometallurgy and solvent extraction processes; Dr. T. J. O'Keefe, Professor of Metallurgical Engineering at the University of Missouri at Rolla, whose expertise is electrometallurgy; Dr. W. Opie, President for Research and Development. AMAX Corporation, whose expertise is extractive metallurgical techniques applied to secondary materials; Mr. A. Mehta, a consultant for Phoenix Metals, whose expertise is environmental concerns and waste processing technology as related to the electroplating industry; and Mr. J. Downey, a private consultant whose expertise is development of pilot scale studies.

The recommended flowsheets formulated by the advisory and review team were investigated at a bench scale level to ascertain applicability or non-applicability of potential unit operations. A flowsheet was developed that had several feasible alternative unit operations. Laboratory demonstrations were performed for each unit operation and each alternate unit operation. A test assembly was developed to treat 75-100 pounds of sludge material per day. Preliminary testwork was conducted at the large scale during Phase I of the project.

The second phase objectives were to investigate potential alternate unit operations identified in Phase I; further test the assembly developed in Phase I; develop long-term continuous test data for the unit operations; and delineate potential process and materials handling problems.

Phase II of the study was conducted by the Montana College of Mineral Science and Technology at two locations; at the College laboratories in Butte, Montana, and at an industrial site in Camarillo, California. Large scale testwork was performed at the industrial site in California. The studies included: leaching, solvent extraction, chromium oxidation and chromium precipitation. Continuous long-term solvent extraction testwork and precipitation studies were performed at the College's laboratories in Butte.

This report is a summation of the results of studies conducted over the period July 1, 1983 until September 30, 1984.

SECTION 2

CONCLUSIONS

2.1. LABORATORY TEST PROGRAM

A laboratory test program has been conducted to support the development of an appropriate flowsheet made up of unit operations designed to accomplish the stated objective of separation and metal value recovery from mixed metal hydroxide sludge materials. The laboratory test program was based on a comprehensive review of current literature; discussions with consultative experts in the field of extractive metallurgy; and previous experimental research conducted at Montana Tech Foundation. Flowsheets were designed based on the inputs gained from the above sources and modified as dictated by the laboratory test program.

The flowsheets that resulted from the Phase I study were based on the treatment of a mixed metal sludge material containing significant concentrations of metal values: copper, nickel, zinc, and chromium, and variable concentrations of other elements that were not considered recoverable as marketable products but which required removal in order not to contaminate the metal value products, e.g., iron, aluminum, and calcium. The developed flowsheets are not an unalterable sequence of operations; alternatives do exist and will be discussed in the body of this report. As is often the case, unit operations may be accomplished by several different technical approaches; e.g., the unit operation of chromium oxidation may be accomplished by use of chemical oxidation reagents or by use of electrochemical cells. The choice is usually based on efficiency and economic considerations.

Another important point concerning the development of the flowsheets is that only commercial process unit operations and commonly used reagents were considered. That is, new developments in the separation of metals from complex solutions have been reported but are not yet adopted commercially. These new developments are reviewed in this report and the consequences of the adoption into the present flowsheet are discussed.

The flowsheets developed for mixed metal sludges are presented in Figures 2.1 (high iron sludges) and 2.2 (low iron sludges). The treatment sequence consists of the following unit operations:

High iron sludges

- Sulfuric acid dissolution of the metal hydroxides.
- Selective precipitation of iron from the solution as a potassium or sodium jarosite ($KFe_3(OH)_6(SO_4)_2$, $NaFe_3(OH)_6(SO_4)_2$).
- Solid-liquid separation of the leach residue and precipitated jarosite solid.
- Selective extraction of copper from the leach solution (with subsequent copper recovery as electrodeposited copper or crystallized copper sulfate) by solvent extraction.
- Extraction of zinc (and residual iron) in preference to chromium and nickel from the leach solution (with subsequent zinc recovery by crystallizing zinc sulfate) by solvent extraction.
- Selective oxidation of chromium ions to form dichromate anions.
- Selective precipitation of chromium from solution (using lead sulfate) as lead chromate. The lead chromate can subsequently be redissolved to produce a concentrated chromic acid solution with the regeneration of lead sulfate.
- Solid-liquid separation of the precipitated lead chromate.
- Selective precipitation of nickel ions from solution as nickel sulfide, nickel hydroxide, or crystallization as nickel sulfate.
- Solid-liquid separation of the nickel compound product.
- Recycle of the resulting purified leach solution to the original leach as make-up water. The unrecycled final leach solution may be discharged or pre-treated by ion exchange before discharge.

Low Iron Sludge

- Sulfuric acid dissolution of the metal hydroxides.

- Solid-liquid separation of the leach solution and unleached residue.

- Selective extraction of copper from the leach solution (with subsequent copper recovery as electrodeposited copper or crystallized copper sulfate) by solvent extraction.

- Selective extraction of zinc and iron by solvent extraction with subsequent zinc recovery by crystallization of zinc sulfate; subsequent iron removal from the organic phase by hydrochloric acid stripping.

- Selective oxidation of chromium ions to form chromium VI anions.

- Selective precipitation of chromium from solution (using lead sulfate) as lead chromate. The lead chromate can subsequently be redissolved to produce concentrated chromic acid solution with the regeneration of lead sulfate.

- Solid-liquid separation of the precipitated lead chromate.

- Selective precipitation of nickel ions from solution as nickel sulfide, nickel hydroxide, or crystallization as nickel sulfate.

- Solid-liquid separation of the nickel sulfide, hydroxide or nickel sulfate.

- Recycle of the resulting leach solution to the original leach as make-up solution. The unrecycled final leach solution may be discharged or pre-treated by ion exchange before discharge.

Each primary unit operation in the flowsheet has been experimentally studied on a bench scale level. Experimental data, discussions of experimental results and studies involving alternative approaches are presented in Section 6 and Appendices 8.2 through 8.14.

Laboratory testwork supports the concept that metal values can be separated and recovered effectively and efficiently from complex mixed metal sludge materials.

2.2. LARGE SCALE TEST PROGRAM

The objectives of the large scale test program were: to size the unit operation equipment so that 75-100 pounds of sludge could be treated per day; to test the unit operations to ascertain if effective and efficient metal value

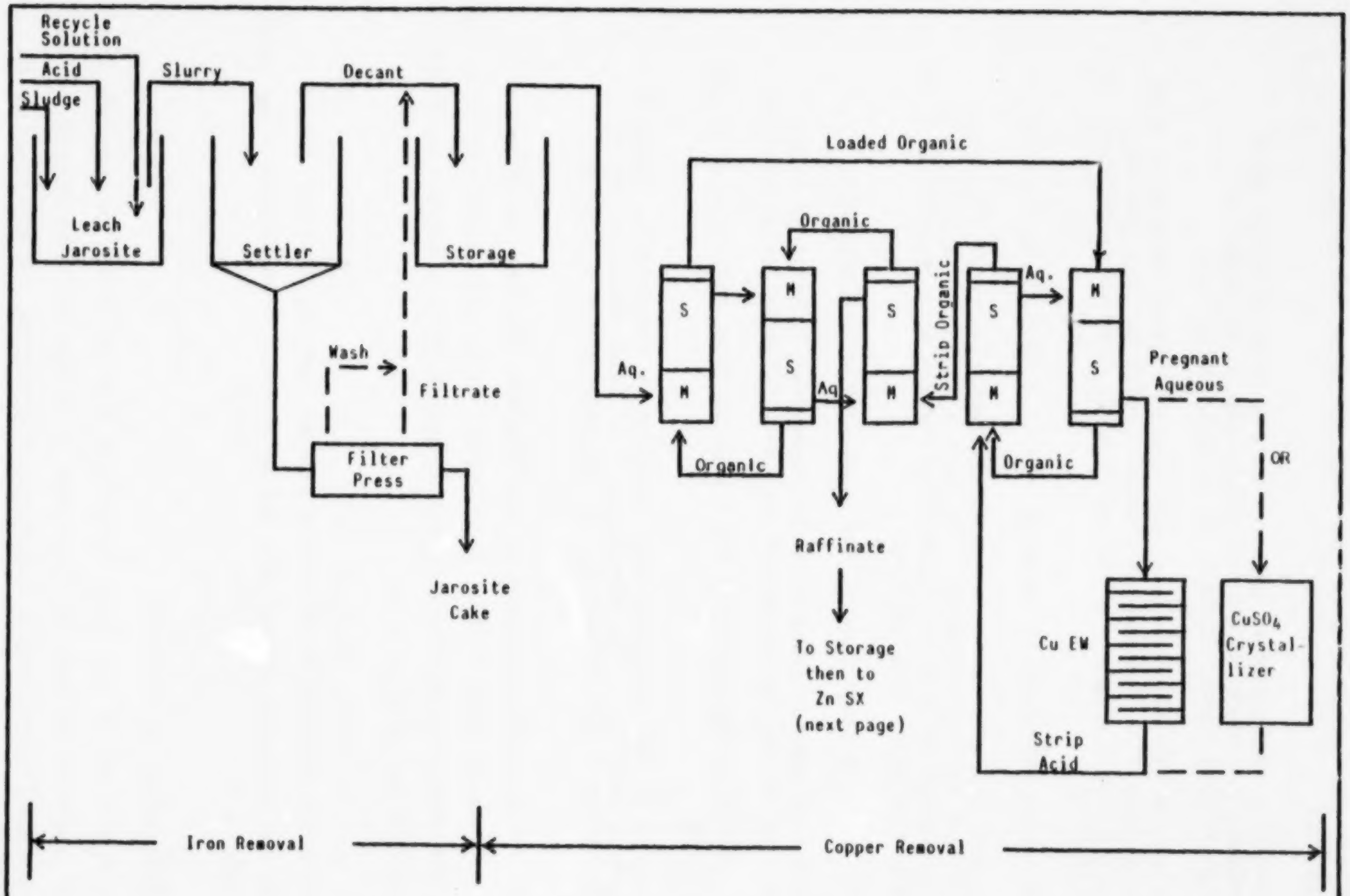
Recycle Solution
Acid
Sludge
Leach Jarosite
Slurry
Settler
Decant
Storage
Wash
Filtrate
Filter Press
Jarosite Cake
Loaded Organic
Organic
Aq.
S
M
Aq
Strip Organic
Organic
Aq.
Organic
Pregnant Aqueous
OR
Raffinate
To Storage then to Zn SX (next page)
Cu EW
$CuSO_4$ Crystal-lizer
Strip Acid
Iron Removal
Copper Removal

Figure 2.1. Flowsheet for treatment of mixed metal hydroxide sludges: High Iron Sludges.

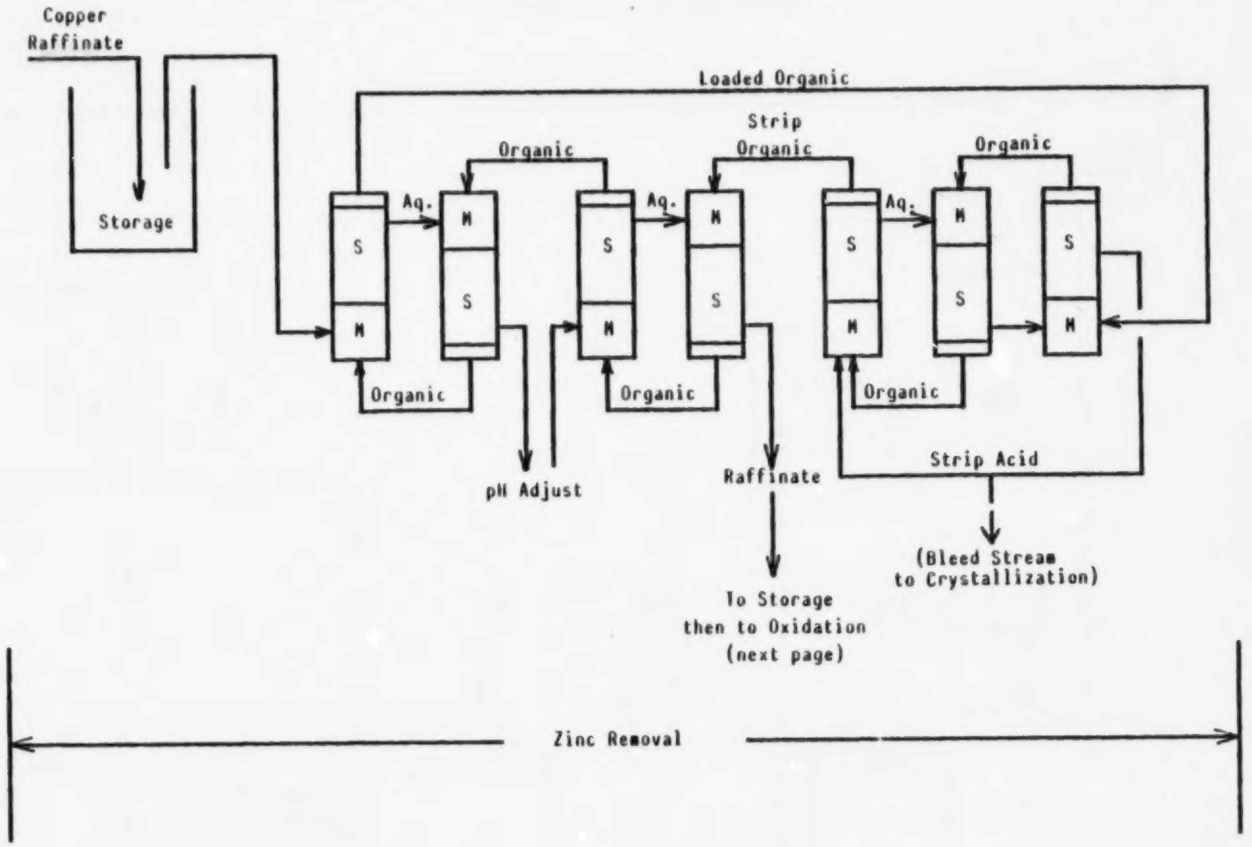
Copper Raffinate
Storage
Loaded Organic
Organic
Strip Organic
Organic
Aq.
Aq.
Aq.
S
M
M
S
S
M
M
S
S
M
M
S
S
M
Organic
Organic
Organic
pH Adjust
Raffinate
Strip Acid
To Storage then to Oxidation (next page)
(Bleed Stream to Crystallization)
Zinc Removal

Figure 2.1. (Continued)

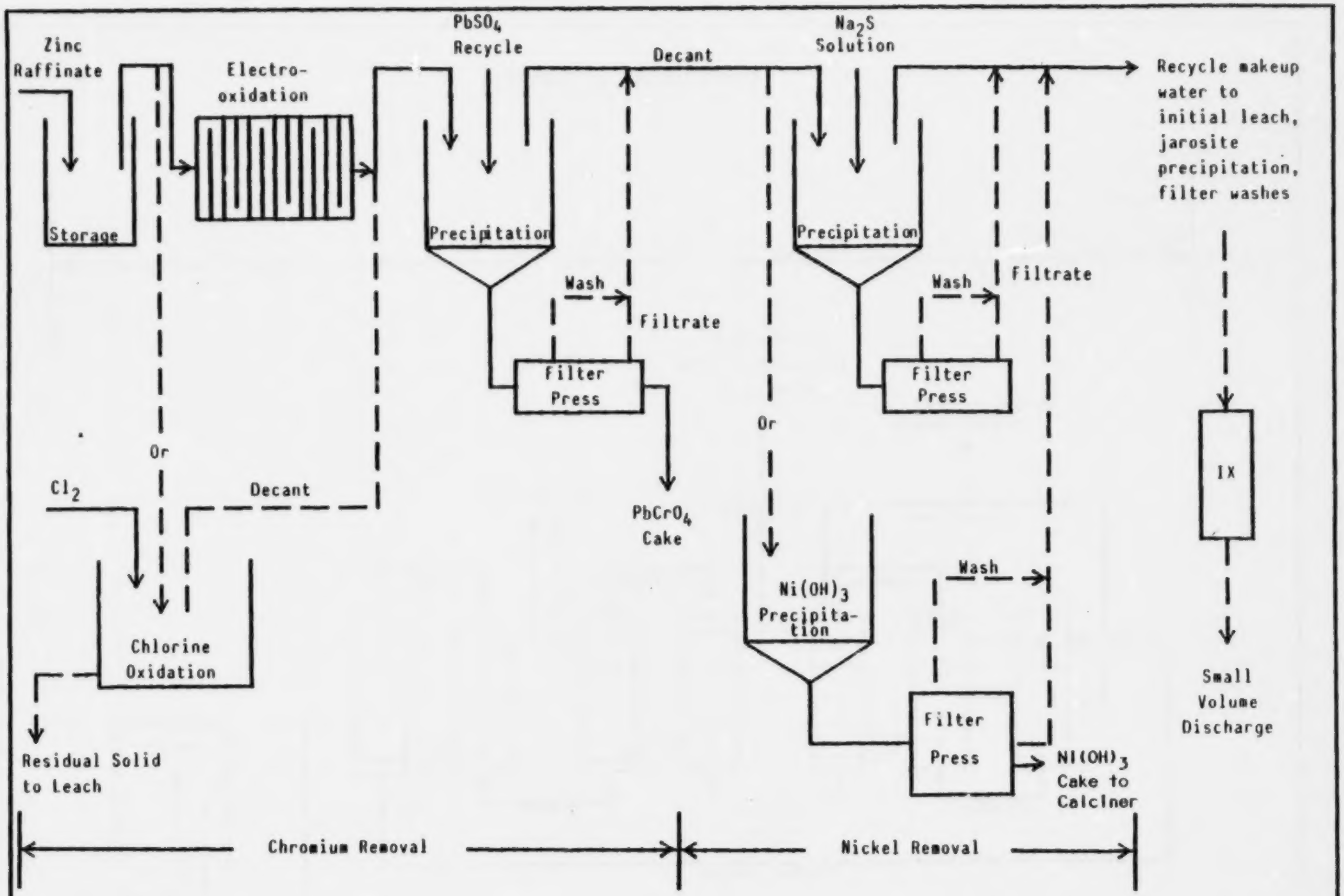
Zinc Raffinate
Storage
Electro-oxidation
Or
Cl$_2$
Decant
Chlorine Oxidation
Residual Solid to Leach
PbSO$_4$ Recycle
Precipitation
Wash
Filtrate
Filter Press
PbCrO$_4$ Cake
Decant
Or
Na$_2$S Solution
Precipitation
Wash
Filtrate
Filter Press
Ni(OH)$_3$ Precipitation
Wash
Filter Press
Ni(OH)$_3$ Cake to Calciner
Recycle makeup water to initial leach, jarosite precipitation, filter washes
IX
Small Volume Discharge
Chromium Removal
Nickel Removal

Figure 2.1. (Continued)

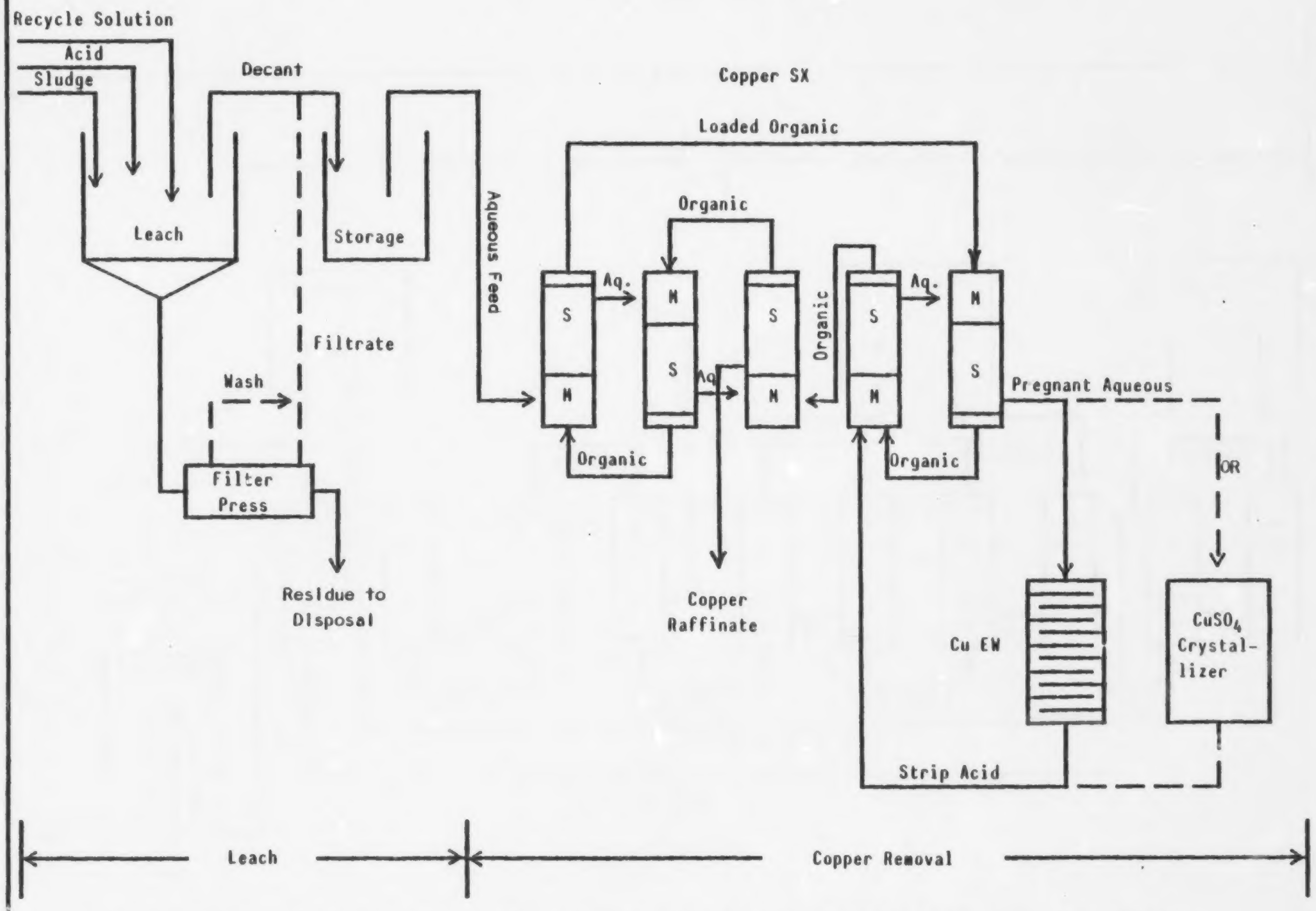
Recycle Solution
Acid
Sludge
Leach
Decant
Storage
Filtrate
Wash
Filter Press
Residue to Disposal
Aqueous Feed
Copper SX
Loaded Organic
Organic
Aq.
S
M
Organic
Aq.
Copper Raffinate
Organic
Aq.
Organic
Pregnant Aqueous
OR
Cu EW
$CuSO_4$ Crystal-lizer
Strip Acid
Leach
Copper Removal

Figure 2.2. Flowsheet for treatment of mixed metal hydroxide sludge: Low Iron Sludge.

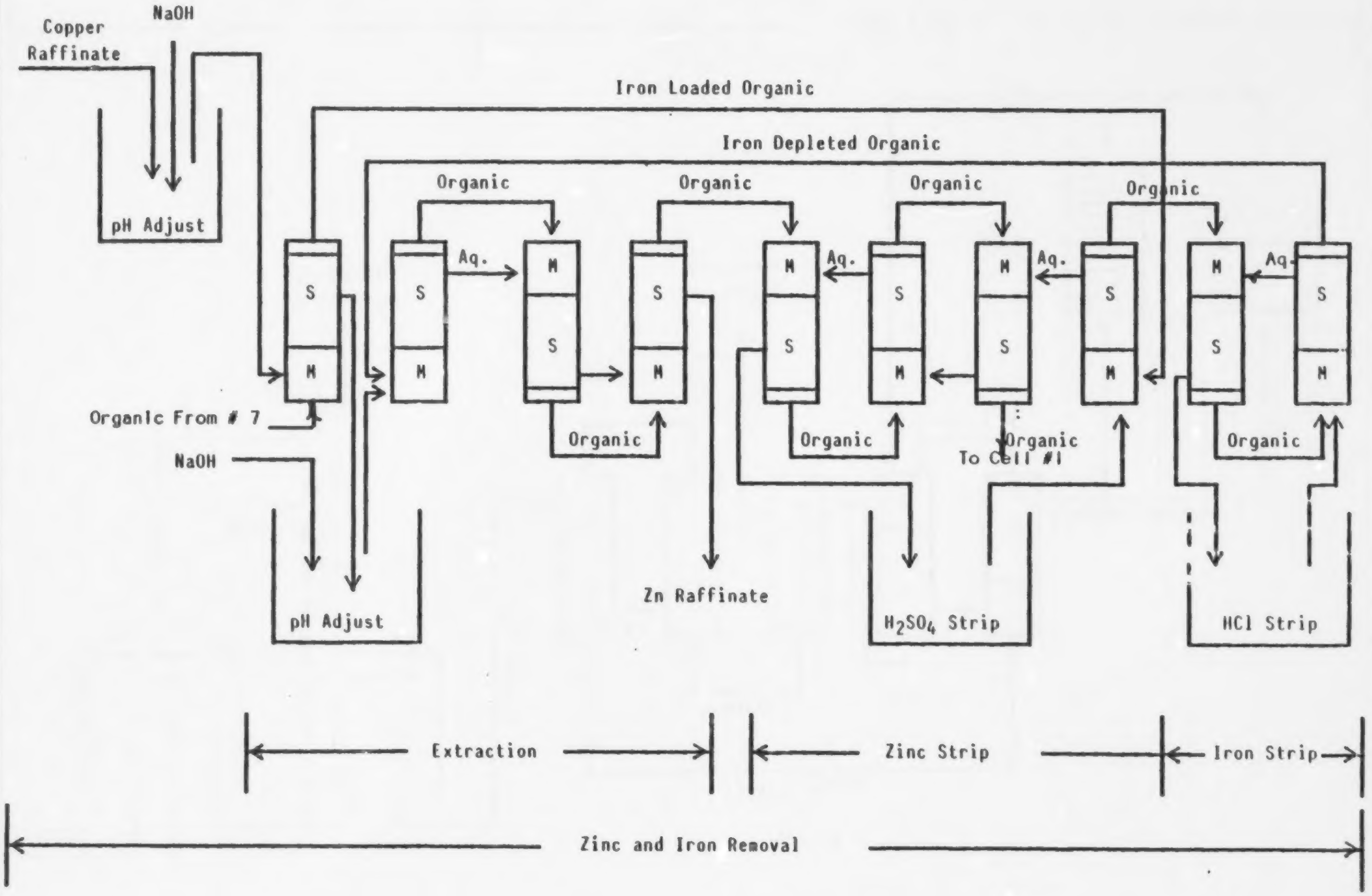
Copper Raffinate
NaOH
pH Adjust
Iron Loaded Organic
Iron Depleted Organic
Organic
Organic
Organic
Organic
Aq.
Aq.
Aq.
Aq.
S
M
Organic From # 7
NaOH
Organic
Organic
Organic To Cell #1
Organic
pH Adjust
Zn Raffinate
H_2SO_4 Strip
HCl Strip
Extraction
Zinc Strip
Iron Strip
Zinc and Iron Removal

Figure 2.2. (Continued)

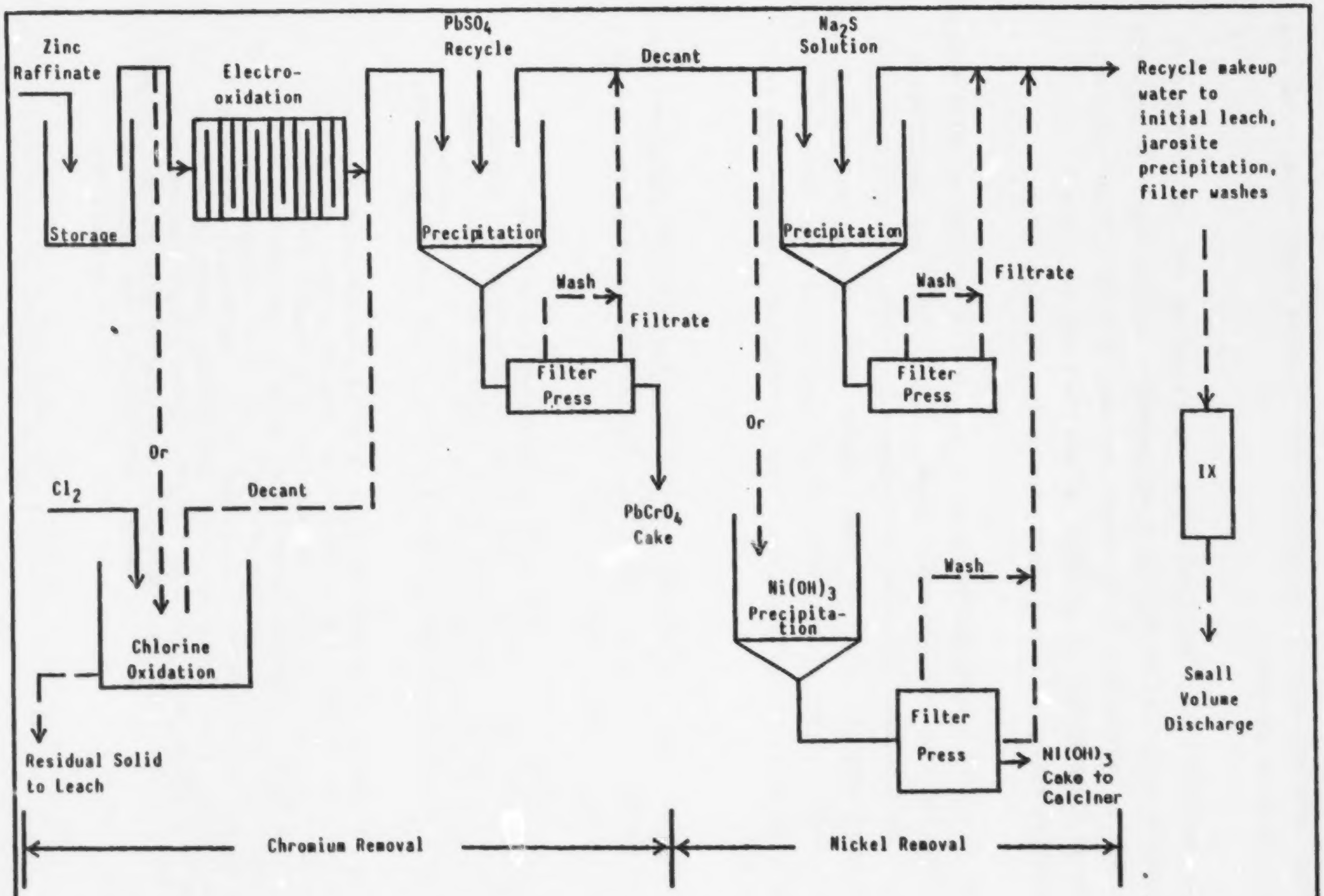
Zinc Raffinate
Storage
Electro-oxidation
Or
Cl_2
Decant
Chlorine Oxidation
Residual Solid to Leach
$PbSO_4$ Recycle
Precipitation
Wash
Filtrate
Filter Press
$PbCrO_4$ Cake
Decant
Na_2S Solution
Precipitation
Wash
Filtrate
Filter Press
Or
$Ni(OH)_3$ Precipitation
Wash
Filter Press
$Ni(OH)_3$ Cake to Calciner
Recycle makeup water to initial leach, jarosite precipitation, filter washes
IX
Small Volume Discharge
Chromium Removal
Nickel Removal

Figure 2.2. (Continued)

extraction and recovery could be achieved; and to determine what chemical and mechanical problems might be associated with treating approximately 200 liters of leach solution per day.

The equipment acquired, fabricated, and assembled for the various unit operations is described in Section 5 and Appendix Section 8.14. It consists of leach vessels, settlers, a filter press, solvent extraction mixer-settlers, chlorine or electrochemical oxidizer, pH monitors and controllers, precipitating vessels, crystallizers, and an ion exchange column.

The flowsheet presented in Figure 2.1 is applicable to mixed metal sludges containing high iron (to 20% iron), copper, zinc, nickel, and low chromium content. The flowsheet presented in Figure 2.2 is applicable to mixed metal sludges containing low iron (<5% iron), copper, zinc, nickel, and high chromium content. Modifications of the flowsheet are possible to treat other iron-chromium metal sludge mixtures. These alternatives are described in Section 6.

A detailed discussion of the large scale individual unit operations are presented in Section 6 and Section 8.13. The conclusions drawn from the test program include the following:

- A sulfuric acid leach operation is effective and efficient in redissolving metal values. The dissolution is rapid and without control problems. Conditions can be specified to achieve greater than ninety percent extraction of all contained metals; between eighty and ninety percent of the starting sludge mass is taken into solution.

- Iron is removed from solution by a jarosite precipitation process. This process allows iron to be removed from an acidic, pH 1.5-2.5, solution as a crystalline compound that is a readily filterable solid product. Elevated temperature, 88-92°C, and chemical pH control are required for the precipitation to be accomplished in a relatively short period of time, 6-8 hours. Mechanical control of the system is not a problem. Over two hundred liters of solution can be treated in an eight hour shift. Solid-liquid separation is readily accomplished by simple settling; pumping most of the cleared solution from the settling vessel; and filtering the remaining slurry using a filter press for cake consolidation and washing.

- An alternate iron removal process appplicable to low iron bearing solutions (<a few grams per liter) is by solvent extraction at low pH with subsequent removal of iron from the organic phase by hydrochloric acid stripping. Iron content in the aqueous leach solution can be effectively lowered to less than 50 ppm. Minimal crud formation results by controlling leach solution pH and by selection of the proper kerosene diluent.

- Copper is effectively and selectively removed from a mixed metal bearing solution by solvent extraction. The copper content can be decreased to low concentrations, <30 mg/l, without appreciable extraction of any other metal specie.

The recovery of copper by solvent extraction requires only three stages of extraction and two stages of strip. Five cells will accommodate the treatment of over 200 liters of leach solution per day (8 hours). Large scale continuous testwork has been performed for periods up to seven hours. Mechanical control of the solution flowrate and interface levels is easily achieved and does not require constant attention.

- Zinc is effectively and selectively removed from a zinc-chromium-nickel bearing solution by solvent extraction. Iron, aluminum and calcium are partially coextracted with zinc. The iron concentration is normally relatively low because of the previous jarosite precipitation process. The solvent extraction process provides a means of removing the residual iron from the leach solution. Subsequently, the iron can be separated from the zinc by a selective stripping process.

Calcium is coextracted from the leach solution by the organic solvent and is stripped from the organic phase along with zinc by sulfuric acid. Calcium forms gypsum in the strip cell and the solid product is filtered from the strip acid. Aluminum is coextracted from the leach solution and is partially stripped with the zinc. Its presence must be considered in the zinc recovery process.

The removal of five grams of zinc per liter of leach solution can be accomplished in four stages of extraction and three stages of strip. Some flexibility to treat higher zinc containing solutions does exist, i.e., control can be exercised over organic/aqueous contact ratio and the concentration of the extracting reagent.

Mechanical control of the solution flowrate and interface levels does not require constant attention. Once the desired flowrates and interface levels are established only minimal operator attention is required. Chemical control of the pH is required. In order to achieve effective zinc removal the pH must be maintained at approximately two. Solution pH control is exercised by adjusting pH after the first two stages of contact.

•Chromium removal is accomplished by first oxidizing the chromium with chlorine gas; electrochemically or potentially with SO_2-O_2 gas mixtures, then precipitating the dichromate ion as lead chromate. Oxidation has been shown to be effective in laboratory scale test reactors. Large scale oxidation testwork using chlorine and an electrochemical reactor have been performed successfully. A recycle system for stripping the oxidized chromium from the leach solution has been operated successfully: the solution is exposed to lead sulfate in an agitated reactor; lead chromate precipitates; the lead chromate product is crystalline and dense and settles rapidly; the solution essentially free of lead chromate solid is pumped from the solids for further treatment for nickel removal; the lead chromate is redissolved in sulfuric acid to form a concentrated chromic acid solution and lead sulfate; the lead sulfate solid is separated from the chromic acid and is recycled to the lead chromate precipitation reactor.

•Nickel can be removed by sulfide precipitation. The reaction is rapid and near quantitative. The pH is maintained in the range 4-5 so hydrogen sulfide is not released. The solid product is readily filterable. Quantitative removal of nickel is not necessary because practically all the final solution can be recycled to the leach-jarosite precipitation unit operation. Therefore, the addition of a deficiency of sulfide (less than the stoichiometric requirement for complete nickel removal) is desirable so that all the added sulfide ions are consumed. Then when the solution is recycled to the acid leach step hydrogen sulfide gas will not be formed. Other alternative nickel recovery unit operations are discussed later. An attractive alternative is the production of nickel oxide (Section 6.4).

2.3. ECONOMIC ANALYSIS

An "order of magnitude" estimate has been performed on the flowsheet presented in Figure 2.1 and expanded in Figure 6.7. The calculated return on investment (ROI) based on the "order of magnitude" estimate is normally considered to be within ±30%(49,50).

Definitions and cost estimation factors are taken primarily from Mular "Mineral Processing Equipment Cost and Preliminary Capital Cost Estimations", and Wood, Chapter 29.1, "Cost of Equipment", and Pratt, Chapter 29.2, "Cost of Process", in the Solvent Extraction Handbook. A summary of the assumptions made and the detailed calculations for treating fifty tons of sludge per day are presented in Section 6.4 and Appendix 8.15. The major assumptions include:

the land and buildings are available; a credit of one dollar per gallon of sludge is allowed; and the tax rate is fifty percent.

The results of the calculations are tabulated for each unit operation in Tables 2.1 and 2.2. The first order estimate for the return on investment is 41 ± 12%.

The largest cost unit operation is recovery of chromium; oxidation is by far the costliest step in recovering useful chromium compounds. There is potentially a new low cost oxidation process now being commercialized for cyanide destruction. The solution oxidizing potential has been shown to be high enough to oxidize nickelous ions in solution to form nickelic hydroxide solid. That level of solution oxidizing power will certainly oxidize chromium ($Cr^{+3} \longrightarrow Cr^{+6}$). The process ($SO_2 + O_2$) is described in Section 6.4. Such a process would not only be less capital intensive but the energy savings would be great. A cost comparison between the flowsheet presented in Figure 2.1 and the flowsheet modified for SO_2-O_2 oxidation is presented in Table 2.3. The difference in the ROI is significant; 41% for the flowsheet presented in Figure 2.1 and 69% for the SO_2-O_2 modified flowsheet.

Another potential alternate treatment process is solvent extraction and electrowinning of nickel, precipitation of chromium hydroxide, and production of chromium oxide (discussed in Section 6.4). A cost comparison between the flowsheet presented in Figure 2.1 and the modified flowsheet is presented in Table 2.4. The difference in the ROI is significant; 41% for the flowsheet presented in Figure 2.1 and 67% for the modified flowsheet.

The detailed cost analyses results presented in Section 6.4 and 8.15 show good potential for an excellent return on investment. Even if a credit is not taken for disposal, two of the modified flowsheets show an income sufficient to offset the cost of the treatment process. It is recommended that further consideration be given to the economic consequences of variations in the chosen unit operations.

TABLE 2.1 PROCESS COST: FIRST ORDER ESTIMATE

Unit Operation	COST ($)			
	Factored Capital Cost Estimate	Annualized Capital Cost	Operation Cost Per Year	Total Cost Per Year
1. Leach, jarosite precipitation	430,800	119,500	223,500	343,000
2. Jarosite storage	390,500	108,200	25,400	133,600
3. Copper solvent extraction, electrowinning	336,100	93,100	205,900	299,000
4. Zinc, residual iron solvent extraction, zinc sulfate crystalization	661,600	183,300	269,700	453,000
5. Chromium oxid., chromic acid production	1,818,200	503,600	407,700	911,300
6. Nickel recovery	231,600	64,200	230,000	294,200
TOTAL COST	3,868,800	1,071,900	1,362,200	2,434,100

See Section 6.4 for details.

TABLE 2.2 PROCESS COST SUMMARY: FIRST ORDER ESTIMATE

Unit Operation	COST ($)						
	Factored Capital Cost/Yr @ 12%		Operation Cost Per Yr		Total Cost Per Yr		Potential value of Product(¢/lb)
	$	¢/lb	$	¢/lb	$	¢/lb	
1. Leach, jarosite precipitation	227,700	4.0*	248,900	4.4*	476,600	8.4*	-
2. Copper SX, EW	93,100	25.0	205,900	55.2	299,000	80.2	60
3. Zinc, residual iron SX, zinc sulfate cryst.	183,300	17.4	269,700	25.7	453,000	43.0	20
4. Chromium oxid., chromic acid production	503,600	66.1	407,700	53.5	911,300	119.6	118
5. Nickel Recovery	64,200	10.9	230,000	39.0	294,200	49.9	172

* per pound of residue solids.

See Section 6.4 for details.

TABLE 2.3. COMPARSION OF FIRST ORDER COST ESTIMATES BETWEEN FLOWSHEETS FOR ELECTROCHEMICAL OXIDATION AND SO_2 - O_2 OXIDATION OF CHROMIUM

Flowsheet	COST ($)				
	FCC	FCAC	Operating Cost/yr	Total Cost/yr	Product Value*
Electrochemical (Table 2.1)	3,868,800	1,071,900	1,362,200	2,434,100	5,643,400
Modified	2,862,900	793,300	1,209,100	2,002,400	5,885,800

$$\text{R.O.I.} = \left[(5{,}885{,}800 - 2{,}002{,}400)/\ 2{,}862{,}900\right](0.50)(100)$$
$$= 69 \pm 20\ \%$$

* Same products in both flowsheets except for nickel: NiS in Table 2.1, NiO in modified flowsheet.

See Section 6.4 for details.

TABLE 2.4. COMPARSION OF FIRST ORDER COST ESTIMATES BETWEEN FLOWSHEETS FOR ELECTROCHEMICAL OXIDATION AND NICKEL SOLVENT EXTRACTION AND RECOVERY.

Flowsheet	FCC	FCAC	Operating Cost Per Year	Total Cost Per Year	Product Value*
Electrochemical	3,868,800	1,071,900	1,362,200	2,434,100	5,643,400
Modified	2,977,300	824,900	1,175,500	2,000,900	5,977,100

$$\mathrm{ROI} = \left[(5{,}977{,}100 - 2{,}000{,}900) / 2{,}977{,}300\right](0.5)(100)$$

$$= 67 \pm 20\ \%$$

* Same products in both flowsheets except for nickel (nickel in modified flowsheet) and chromium (chromium oxide in modified flowsheet).

See Section 8.15 for details.

SECTION 3

RECOMMENDATIONS

The treatment of hydroxide sludge materials for metal value recovery by a series of conventional extractive metallurgical unit operations has been demonstrated. The treatment sequence is selective and effective for recovering copper, zinc, chromium, and nickel. Iron, calcium and aluminum can be extracted from the leach solution and rejected from the system.

The highest cost unit operation in the treatment sequence is oxidation of chromium. Alternatives have been suggested; oxidation by SO_2/O_2 gas mixtures or solvent extraction of nickel, precipitation of chromium(3) hydroxide with subsequent calcining to chromium oxide. Both of these alternatives to the original flowsheet appear to offer a great savings in cost. The alternatives are, however, not presently commercially proven processes. Further research and development studies are necessary to insure applicability to the present system. Specifically the needed research includes:

1. A study of the possibility of oxidizing chromium in a chromium-nickel bearing solution by SO_2/O_2 mixtures. The use of SO_2/O_2 is presently commercially used by INCO to destroy cyanide in waste leach solutions. The oxidizing potential that can be developed by the SO_2/O_2 has been shown to be sufficient to oxidize nickel(+2) to nickel(+3). Therefore, the application of SO_2/O_2 to a chromium-nickel solution appears to have the potential for oxidizing both chromium(+3) and nickel(+2). The envisioned treatment would be carried out at a low solution acidity, i.e., pH 8. The chromium and nickel would both exist as hydroxides. As the oxidization progressed chromium(+6), as chromate, would be soluble; nickel(+2) would be oxidized to nickel(+3) hydroxide and remain as a solid. A solid/liquid separation would then be used to separate the chromium from the nickel. The chromium(+6) solution could be treated as suggested in the previous flowsheets. The separated solid nickel hydroxide could be calcined to nickel oxide.

2. A study to determine the possibility of separating nickel from chromium by solvent extraction using either mixtures of

D_2EHPA-EHO or D_2EHPA-LIX63. Both have been shown previously by other investigators to extract nickel from acidic solutions. Investigations reported in the present study show that the extraction is selective toward nickel, i.e., in a nickel-chromium bearing solution, nickel is extracted but chromium(+3) is not. Therefore, an envisioned treatment would include selective removal of nickel(+2) with subsequent recovery from solution as nickel by electrowinning; followed by precipitation of chromium(+3) hydroxide at a pH of 3-4.5; and then solid/liquid separation with subsequent conversion of chromium hydroxide to chromic oxide by calcining.

It is recommended that a detailed cost analysis be performed on the proposed flowsheets and the potential alternate unit operations. The first order cost estimates presented in Section 6.4 indicate that sludge treatment may be economically attractive. These estimates, therefore, should now be followed by detailed cost projections.

SECTION 4

MATERIALS AND METHODS

4.1. SLUDGE CHARACTERIZATION

4.1.1. Starting Sludge Material

Experimental analytical procedures and sample preparation techniques are presented in Appendix 8.1. For the most part, Induction Coupled Plasma Spectrophotometry (ICP) was used for determination of elemental concentrations in solutions.

4.1.1.1. Phase I Material

Sludge materials were obtained from three different industrial sources. The material was packed in fifty-five gallon barrels by the producer and shipped to Butte, Montana. The sludges were, in most cases, mixed metal hydroxide materials (Table 4.1). A portion of the supplied material was electroplating cell bottom sludge rather than precipitated hydroxide sludge, e.g., 6, 7, and 8. The solids content of all the sludges ranged approximately 20-35 weight percent, e.g., Table 4.2.

Even though the sludge materials were only 20-35 percent solids they could be handled like solids, i.e., they could be broken into smaller pieces without release of free water. The material could be broken up into small pellet-like chunks (approximately one-eighth inch diameter) by use of a laboratory hand mixer.

X-ray diffraction patterns of dried sludge showed the material to be amorphous as is typical of precipitated hydroxides.

TABLE 4.1. MIXED METAL SLUDGE COMPOSITION OF AS-RECEIVED SLUDGE

Sample No.	Sludge Source	Composition (%) in Solids*								
		Cu	Fe	Zn	Cr	Ni	Cd	Al	Ca	P
	Barrel 1									
544 A		8.06	18.21	11.73	1.20	5.59	0.74	2.92	1.00	4.13
544 B		7.87	17.70	11.46	1.19	5.55	0.72	2.78	1.19	4.51
545 A		7.56	19.16	10.98	1.11	5.30	0.70	2.68	1.01	4.29
545 B		7.69	18.71	11.11	1.14	5.44	0.71	2.75	1.00	4.44
546 A		7.63	17.19	11.58	1.13	5.41	0.71	2.71	2.47	4.49
546 B		8.24	18.65	11.94	1.23	5.86	0.77	2.94	1.08	4.98
	Barrel 2									
927		5.66	15.90	10.76	1.23	6.11	0.66	4.64	1.41	2.79
928		5.61	15.75	10.67	1.23	6.07	0.66	4.60	1.38	2.93
929		5.84	16.58	11.18	1.29	6.31	0.69	4.83	1.46	3.13
975		5.69	15.17	10.15	1.03	4.16	0.52	3.94	0.76	4.30
976		5.11	14.32	9.46	0.98	3.86	0.48	3.74	0.80	4.39
	Barrel 5									
227		2.41	11.33	8.40	1.36	5.08	0.39	4.05	1.08	----
228		2.41	11.88	8.45	1.35	4.80	0.41	4.15	1.00	----
229		2.48	11.65	8.75	1.35	5.08	0.40	4.55	1.10	----
986		2.46	12.68	8.72	1.10	3.69	0.29	5.23	1.04	2.03
987		2.26	12.18	9.18	1.08	3.52	0.23	4.87	1.07	2.66
988		2.54	13.34	9.84	1.18	3.84	0.25	5.74	1.11	2.40
989		2.41	13.11	8.66	1.16	3.65	0.30	5.63	1.08	2.46
	Barrel 6									
1036		0.12	<D. L.	0.06	0.45	37.48	<D. L.	<D. L.	0.37	<D. L.

TABLE 4.1. CONTINUED

Sample No.	Sludge Source	Composition (%) in Solids								
		Cu	Fe	Zn	Cr	Ni	Cd	Al	Ca	P
1037	Barrel 7	0.16	0.004	0.18	0.54	30.31	<D. L.	0.11	1.02	<D. L.
1038	Barrel 8	1.15	0.30	0.02	22.70	1.16	<D. L.	0.50	1.31	0.43
1039	Barrel 9	0.02	0.14	<D. L.	9.22	0.01	<D. L.	9.96	0.41	<D. L.
1040	Barrel 10	0.34	1.94	0.02	13.14	1.47	<D. L.	2.38	1.13	<D. L.
1041	Barrel 11	0.17	D. L.	0.71	0.76	37.75	<D. L.	0.07	1.52	<D. L.
1222 2135	Barrel 12	1.47 1.45	17.33 17.05	5.82 4.54	3.38 4.50	6.88 7.49	0.09 0.28	<D. L. 2.81	3.05 0.57	1.82 2.17
1223	Barrel 13	1.26	20.26	7.95	0.80	7.82	0.10	<D. L.	3.47	2.11
1224	Barrel 14	2.76	15.54	10.68	1.34	10.54	0.23	<D. L.	5.11	2.71

TABLE 4.1. CONTINUED

Sample No.	Sludge Source	Composition (%) in Solids								
		Cu	Fe	Zn	Cr	Ni	Cd	Al	Ca	P
	Barrel 14 (cont.)									
1700		2.29	17.42	11.65	1.14	9.40	0.39	1.97	Calcium	3.19
1701		2.19	18.49	10.32	1.05	8.76	0.42	2.25	Channel	2.87
1702		2.25	18.70	10.41	1.09	8.82	0.43	2.30	not	3.03
1703		2.05	18.26	10.57	1.04	8.35	0.46	2.27	Operative	2.85
1820		2.10	18.40	9.24	1.03	8.70	0.40	2.18	↓	2.19
1821		2.19	19.55	9.48	1.07	8.56	0.41	2.33		2.22
1822		2.14	20.05	9.16	1.10	7.12	0.47	2.48		2.31
	Barrel 15									
1225		1.59	17.52	9.64	1.75	10.20	0.32	<D. L.	5.94	1.26
	Barrel 16									
2136		1.70	15.68	16.92	1.51	3.83	0.37	3.70	1.38	1.26
	Barrel 17									
2137		4.00	15.20	10.53	4.90	3.89	0.16	2.62	0.98	2.23
	Barrel 18									
2138		6.78	17.19	6.81	7.13	2.31	0.01	2.44	0.23	3.19
	Barrel 19									
2139		1.91	18.68	13.31	2.67	4.56	0.15	2.28	0.97	1.67

---

* Sludge solid content varied from approximately 20-30 weight percent solids.

TABLE 4.2. MOISTURE CONTENT OF AS-RECEIVED MIXED METAL SLUDGE

Sludge Source	% H_2O	% Solids
Barrel #1	76.34) 77.69) 76.81 76.20) 77.01)	23.19
Barrel #2	77.62) 77.85) 77.53 76.90) 77.67)	22.47
Barrel #5	76.39) 76.59) 76.39 76.13) 76.44)	23.61
Barrel #6	77.46	22.54
Barrel #7	76.23	23.77
Barrel #8	82.45	17.55
Barrel #9	83.89	16.11
Barrel #10	79.41	20.59
Barrel #11	82.25	17.75
Barrel #12	76.69	23.31
Barrel #13	79.50	20.50

TABLE 4.2. CONTINUED

Sludge Source	% H_2O	% Solids
Barrel #14	81.34) 82.13) 81.43) 81.80) 81.87 82.75) 82.45) 81.18)	18.13
Barrel #15	76.69	23.31
Barrel #16	70.65	29.35
Barrel #17	74.19	25.81
Barrel #18	69.47	30.53
Barrel #19	77.48	22.52

A water leach of starting sludge material showed very little redissolution of metal values, e.g., sludge from barrel number eight (Sample No. 1355) showed very little metal dissolution: 0.6% Cr, 1.3% Fe, 1.4% Ni, 1.9% Cu, 2.2% Al (leach conditions: 10% solids, 0.5 hr., ambient temperature).

4.1.1.2. Phase II Material

The material used in the Phase II study was obtained from the local California company where the test assembly was located. The required test material was obtained as needed from current daily sludge production. Example analyses are presented in Table 4.3. The sludge was primarily a high chromium-high nickel-low iron material. The solid content varied between 16-30 percent. In some cases, the sludge material was doped with copper and zinc sulfate for testwork requiring solutions containing iron, nickel, chromium, copper and zinc.

4.1.2. Methods of Analysis

A detailed summary of sample preparation and analytical procedure used to chemically characterize the sludge materials is presented in Appendix Section 8.1. The sample dissolution procedure used was a perchlorate fuming technique: the aqueous solution analytical technique used was atomic absorption and induction coupled plasma spectrophotometry. Montana Tech Foundation was supplied with a set of solutions by EPA to verify the laboratories' analytical capabilities. The EPA solution analytical verification results are reported in Appendix Table 8.1. and discussed in Section 8.1. All aqueous leach solutions, raffinates and organic analyses were performed using induction coupled plasma spectrophotometry.

4.2. REAGENTS

Chemical reagents used throughout the study were either technical or reagent grade. They included: acids; bases; solid compounds such as lead sulfate, sodium sulfide. Tap water was used in the large scale testwork;

TABLE 4.3. MIXED METAL SLUDGE COMPOSITION FOR CAMARILLO SLUDGE MATERIAL

Sample No.	Solid Content (%)	Composition (%) in Solids								
		Cu	Fe	Zn	Cr	Ni	Al	Pb	Ca	P
3177	16.5	0.1	5.3	0.5	5.0	32.0	<0.1	-	-	-
3183	25.0	0.1	5.8	0.3	13.3	17.9	<0.1	<0.1	-	-
3184	25.0	0.1	4.8	0.3	11.4	19.7	<0.1	<0.1	-	-
3291	26.5	0.1	4.5	0.4	9.1	34.4	<0.1	<0.1	0.4	-
3301	28.7	0.1	4.7	0.1	11.7	23.3	<0.1	<0.1	0.8	-
3332	26.7	0.1	2.4	0.3	10.5	26.1	<0.1	<0.1	0.9	-

deionized water was used in small scale kettle testwork and in all reagent dissolution and dilution procedures.

Solvent extraction reagents were supplied by vendors and were the same reagents supplied to their commercial customers. The reagents were sometimes donated to the project and at other times were purchased. The reagents included: LIX-64N, LIX-622, LIX-70 (Henkel Corporation); D_2EHPA and Alamine 336 (Mobil Corporation); ACORGA 5100 (ACORGA Corporation); DNNSA and XB-1 (King Industries). These reagents were diluted to the desired strength by use of KERMAC 470B and KERMAC 510B Kerosene (Kerr-McGee Corporation).

Ion exchange resins were supplied by Rohm and Haas and were the same resins supplied to their industrial customers. Those resins used in this study included: a weakly basic anion cation exchanger IRA-94; a strongly basic anion exchanger IRA 900; and a strongly acid cation exchanger IRA 200.

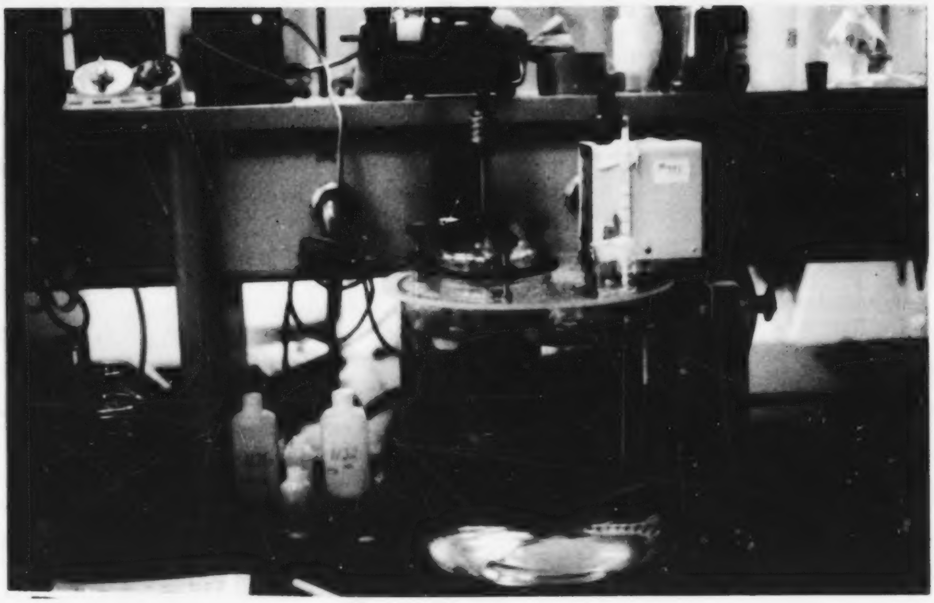

Figure 5.1. Laboratory leach system.

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SECTION 5

EXPERIMENTAL PROCEDURES

5.1. LEACH AND PRECIPITATION STUDIES

The leach and precipitation studies were initially conducted in one liter thermostated reaction kettles. A typical set-up is presented in Figure 5.1. The reaction kettles allowed testwork to be controlled over a wide range of experimental conditions. A two level factorial design matrix was utilized in order to minimize the number of experimental tests necessary to establish appropriate experimental conditions for the larger scale testwork. Experimental conditions investigated for the leach and jarosite precipitate testwork included: reaction temperature; reaction time; acid and reagent concentration; solution Eh; agitation rate; and solid/liquid ratio.

The conditions for each individual experimental study were based on the set of conditions specified in the design matrix table. For example, the experimental leach study procedure included: selecting and blending a starting sludge sample; splitting a sample for determination of moisture content; splitting a sample for determination of elemental content; weighing the sludge sample and placing in the reaction kettle; setting the experimental temperature (thermostated water bath); initiating the study by addition of concentrated sulfuric acid; diluting the sample to the desired volume; setting the agitation rate; adjusting pH; sampling the solution as a function of time for analysis; running the test for designated time; removing the reaction kettle from the bath vessel; separating the solid from liquid by vacuum filtration and sampling the solution and sometimes the solid for analysis. Based on the results from a series of design matrix tests and further optimization testwork, a standard leach procedure was adopted; i.e., one-half hour; temperature 40-55°C; acid concentration, equivalent to a weight of 100% of the solid content of the sludge; a sludge/liquid ratio of 0.8; and an agitation rate to completely suspend all particles in the solution phase.

Jarosite precipitation studies followed the leach studies. Testwork was performed to determine the appropriate conditions for jarosite precipitation of iron from the leach solutions and the appropriate conditions for jarosite precipitation in the presence of leach residue solids (designated in-situ precipitation). The procedure was to first leach the sludge material under standard conditions then to either filter the solids from the solution or to leave the solids in the solution and to then adjust the conditions to permit jarosite to form. The results of these studies are presented in Section 6.2.2. and Appendix 8.3.1.

The small-scale testwork was followed by leach and jarosite precipitation experiments in a ninety-liter polypropylene reaction vessel; followed by testwork in a full-scale 270-liter polypropylene reaction vessel. (The results of these experiments are presented in Section 6 and Appendices 8.3.1 and 8.13. The experimental procedure for the large-scale testwork was similar to the laboratory testwork. The experimental conditions for the large-scale testwork were based on the best small scale results. A schematic drawing of the leach-jarosite reaction vessel is presented in Figure 5.2; a pictoral depiction is presented in Section 8.14.

The experimental procedure for the large scale high iron bearing sludge testwork included: sludge blending and sampling; feeding into the 270 liter reaction vessel; adding concentrated sulfuric acid slowly to break up the solid chunky material; diluting to the desired volume (this process raised the temperature to 50-60°C); placing a heavy duty stainless steel agitator in the reaction chamber to suspend the solids in solution; reacting for one-half hour; raising the temperature to approximately 90°C (by two 6,000 watt quartz immersion heaters) adjusting solution pH conditions to 2.2-2.6 using KOH; adding K_2SO_4 so that the stoichiometry and reaction conditions were appropriate for jarosite precipitation; reacting for 4-6 hours (pH periodically adjusted); sampling hourly to determine the iron content of the solution; adding dropwise (at about 1,000 cc/hr for the last two hours of the test) hydrogen peroxide to

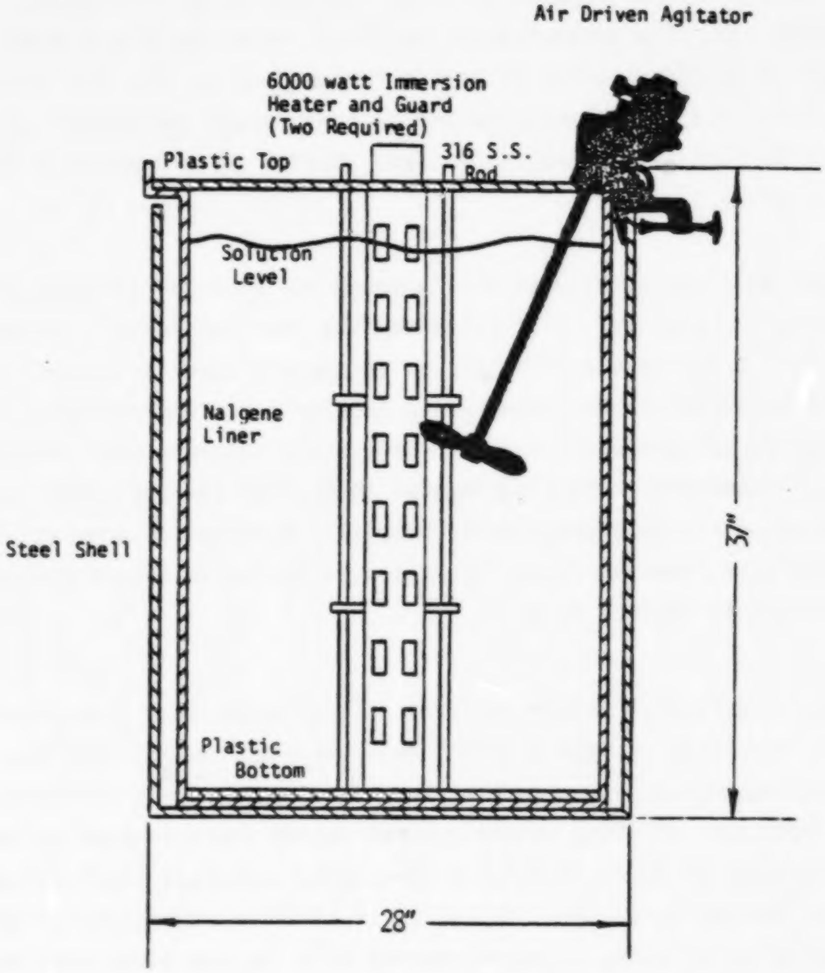

Air Driven Agitator
6000 watt Immersion
Heater and Guard
(Two Required)
Plastic Top
316 S.S.
Rod
Solution
Level
Nalgene
Liner
Steel Shell
Plastic
Bottom
37"
28"

Figure 5.2. Leach-jarosite reaction vessel (Cross section view).

oxidize the ferrous iron; pumping the solution to a storage tank for solid/liquid separation by settling (required about one-half hour for complete settling); pumping the solution from the settling tank to a feed tank for the following SX unit operations; and pumping the jarosite loaded slurry, about 40% solids, to the LASTA filter press (described in Section 8.5) for final solid/liquid separation. The filter cake was sampled to determine moisture content and to determine if the solids would pass the EP Toxicity Test.

The experimental procedure for the large scale low iron bearing sludge excluded the jarosite precipitation unit operation. The sludge material was blended; fed into the reaction vessel; sulfuric acid solution was added and the leach reaction was initiated and conducted for one-half hour. The resulting slurry was pumped to the LASTA press and filtered using a filter aid.

5.2. SOLVENT EXTRACTION

Studies were conducted to investigate the potential application of solvent extraction (SX) to selectively extract and recover copper, zinc, iron, and nickel. The experimental methodology consisted of first conducting batch shake tests on a small scale (125-250 cc) in separatory funnels. These preliminary experiments were followed by continuous testing in a Bell Engineering 600 cc mixer-settler test rack; followed by full-scale continuous testing in a Reister one-gallon mixer-settler test rack.

The hand shake tests were performed to establish: the influence of reagent selectivity for a particular element; the influence of aqueous phase pH, temperature, time, diluent concentration, and reagent concentration, on chemical specie exchange and phase separation between the organic and aqueous phase during extraction and during stripping operations. The shake tests provided a means for selecting appropriate conditions under which to start the continuous testwork.

The small scale test rack consisted of ten 600 cc mixing chambers and ten 600 cc settling chambers. A combination of one to ten cells could be assembled so the counter-current flow, and contact and settling of the organic and aqueous phases were controllable. Solution flow rates (to 50 cc/minute) between mixers and settlers and the organic-aqueous interface positions were controllable. Therefore, retention time and organic/aqueous phase ratio were controllable.

The larger scale test rack consisted of ten one-gallon mixing chambers and ten one-gallon settling chambers. Solution flow rates were controllable up to 500 cc/minute. Details of the solvent extraction system are presented schematically in Figures 5.3 and 5.4.

Two large scale test racks were available for the project. Individual cells were connected in a variety of arrangements to study both copper and zinc extraction from the aqueous phase and to study stripping characteristics of the metal values from the organic phases.

5.2.1. Copper Solvent Extraction

5.2.1.1. Separatory Funnel Shake Test

The small scale separatory funnel (125 and 250 cc) shake tests were used to investigate the applicability of a specific extracting reagent to the mixed metal aqueous solutions. The experimental procedure used in the testwork followed the sequence; the pH of the aqueous phase was adjusted to the desired value; an organic phase was prepared containing a specific extracting agent dissolved in a kerosene solvent; the two phases were added to the separatory funnel in the desired organic to aqueous ratio (O/A); the separatory funnel was stoppered and agitated for a specified time; the agitated mixture was allowed to separate into two distinct phases and each phase was sampled for analysis; the pH of the aqueous phase was measured to establish the equilibrium pH.

5.2.1.2. Large Scale Test

The large scale testwork was performed in the Reister testrack. Preliminary continuous tests were performed in the smaller Bell Engineering testrack to establish proper mixing and settling residence time and to determine if muck or crud formation would be a problem.

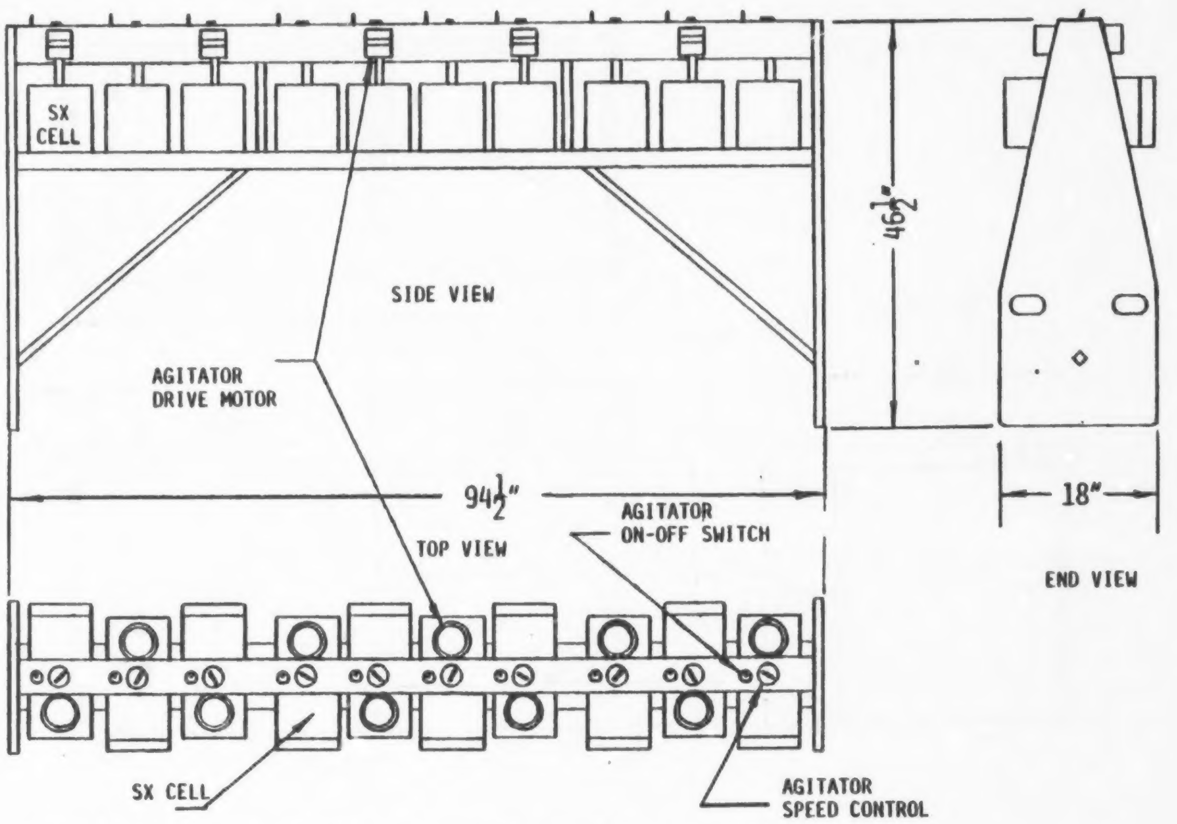

SX CELL
SIDE VIEW
AGITATOR DRIVE MOTOR
46½"
94½"
TOP VIEW
AGITATOR ON-OFF SWITCH
18"
END VIEW
SX CELL
AGITATOR SPEED CONTROL

Figure 5.3. Reister one-gallon mixer-settler system: Testrack details.

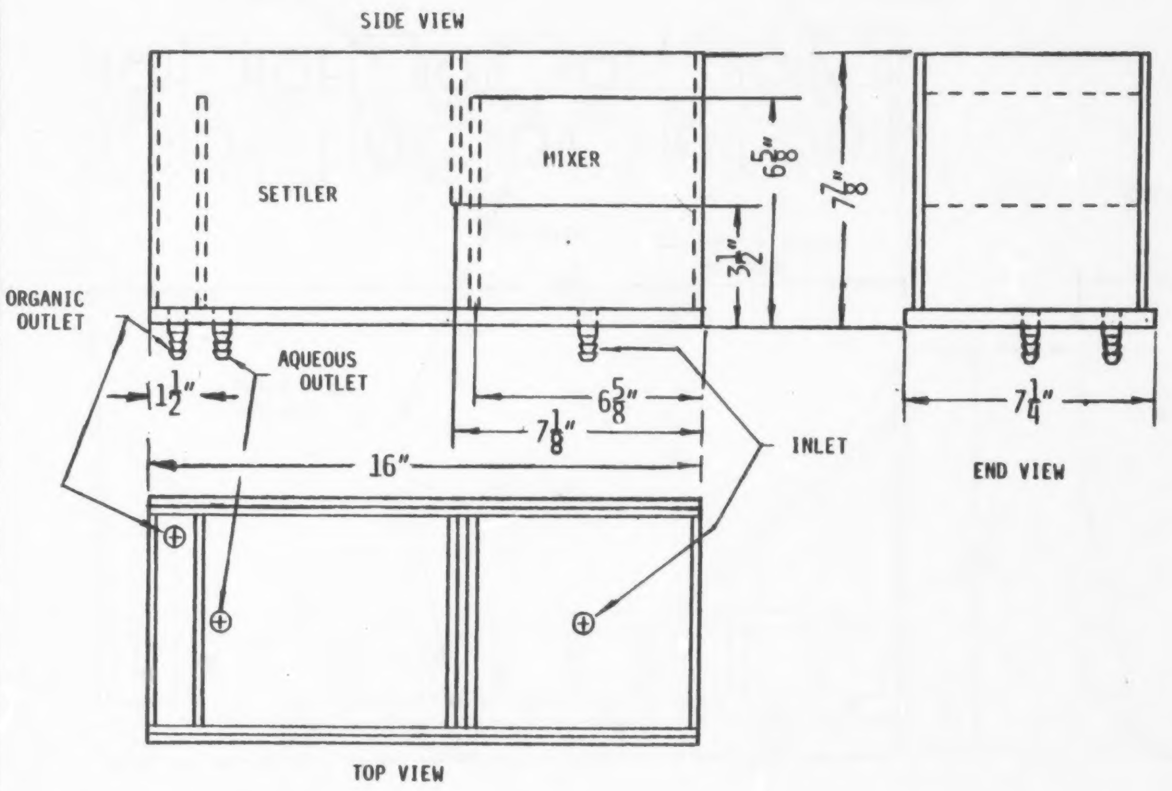

SIDE VIEW
SETTLER
MIXER
ORGANIC OUTLET
AQUEOUS OUTLET
INLET
$1\frac{1}{2}''$
$16''$
$6\frac{5}{8}''$
$7\frac{1}{8}''$
$3\frac{1}{2}''$
$6\frac{5}{8}''$
$7\frac{7}{8}''$
$7\frac{1}{4}''$
END VIEW
TOP VIEW

Figure 5.4. Reister one-gallon mixer-settler system: Individual mixer-settler cell.

The procedure used in the testwork followed the sequence: a decision was made on the number of extraction stages (one and two investigated) and stripping stages (usually two stages); the stages were connected so that a countercurrent aqueous-organic flow pattern was established (Figure 5.5); the cells were loaded with the proper organic to aqueous ratio (O/A); solution flow was initiated at desired flowrate (up to 500 cc/min.); samples of aqueous raffinate and strip acid into and out of the system were pulled as a function of time; pH of the raffinate was monitored.

5.2.1.3. Organic Degradation Testwork

Extended exposure testwork was conducted to determine if the organic phase showed extensive degradation and deterioration with continued use. The Bell Engineering SX rack was used for this testwork. Three stages of extraction and two stages of strip were investigated. The test conditions were similar (but for extended times) to the large scale testwork; 50 cc/min. (250 cc/min. large scale testrack); O/A = 1 for both organic loading and stripping; pH = 1.75; temperature, 50-55^{o}C; and strip acid 200 gpl H_2SO_4.

The procedure used in the testwork was to expose a fixed volume of organic (3 liters) to a large quantity of copper bearing leach solution. The organic solution was repeatedly exposed to copper loading and stripping. The effectiveness of the organic phase was determined by closely monitoring the element concentrations in the raffinate solution and by sampling the organic phase after approximately every forty liters of aqueous contact. The organic sample was stripped twice with 200 gpl sulfuric acid then exposed to a standard leach solution (two contacts). The effectiveness of the organic extractant was determined by its ability to remove Cu selectively from the standard solution.

5.2.2. Zinc Solvent Extraction

5.2.2.1. Separatory Funnel Shake Test

The small scale testwork was conducted using the same procedure outlined in Section 5.2.1.1. D_2EHPA was the only extractant investigated for zinc

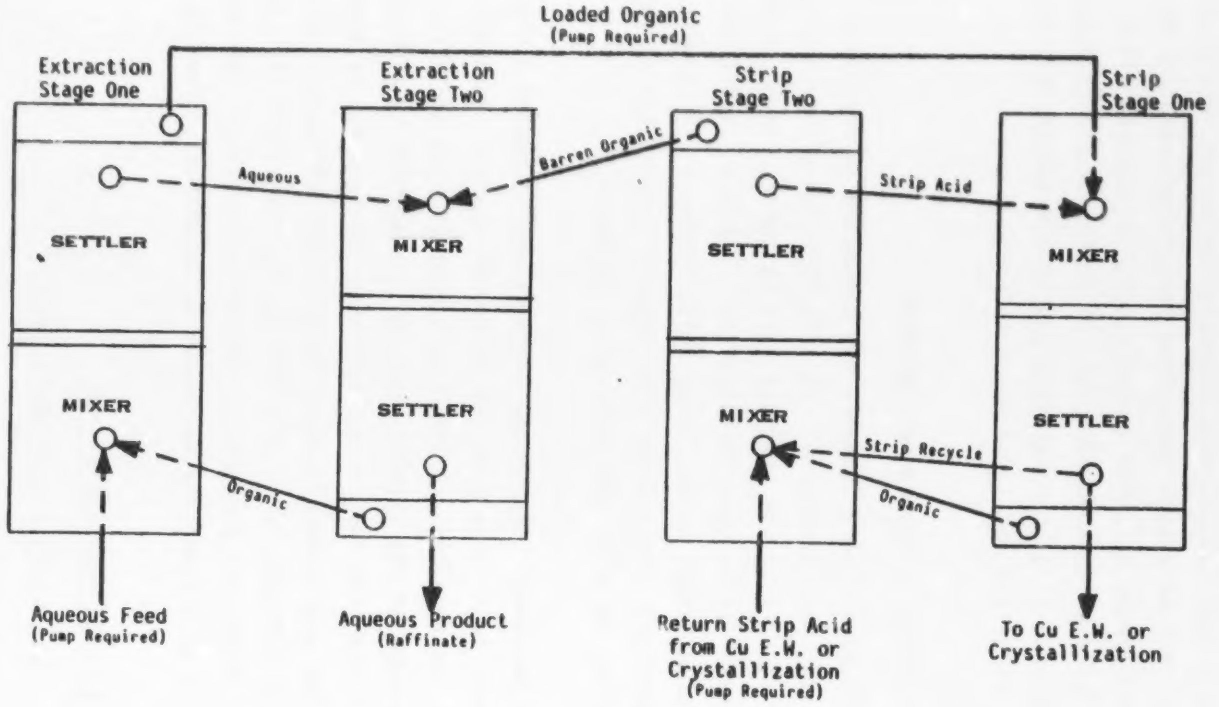

Loaded Organic
(Pump Required)
Extraction Stage One
Extraction Stage Two
Strip Stage Two
Strip Stage One
SETTLER
MIXER
Aqueous
MIXER
SETTLER
Barren Organic
SETTLER
MIXER
Strip Acid
MIXER
SETTLER
Organic
Strip Recycle
Organic
Aqueous Feed
(Pump Required)
Aqueous Product
(Raffinate)
Return Strip Acid from Cu E.W. or Crystallization
(Pump Required)
To Cu E.W. or Crystallization

Figure 5.5. Copper solvent extraction flow pattern.

extraction. Phase separation proved to be a problem for high iron bearing solutions but not so for low iron-high zinc aqueous solutions.

5.2.2.2. Large Scale Test

Intermediate scale continuous testing in the Bell system showed that calcium was extracted concurrently with the zinc and that it precipitated in the strip cells as gypsum. Procedural techniques were worked out to eliminate the transfer of solid gypsum back to the extraction stages. Testwork was conducted using a variable number of stages of extraction and stripping.

Phase I Study

Large scale testing was conducted in seven cells of the Reister testrack. The procedure used in the testwork was developed on the small continuous Bell system. The procedure consisted of: connecting the stages so that four extraction stages and three strip stages were used (Figure 5.6); the cells were loaded with the proper organic to aqueous ratio (O/A = 1 or O/A = 3); solution flow was initiated at the desired flowrate (up to 500 cc/min.); samples were taken (and pH monitored) of raffinate from stage two and stage four and from the strip acid into and out of the system as a function of time; phase interfaces were observed for muck or crud formation.

Phase II Study

Large scale testing was conducted in ten cells of the Reister testrack to investigate a potential flowsheet allowing for low iron bearing solutions to be treated by solvent extraction without prior jarosite precipitation. The concept for the study was that iron could be removed from the leach solution at low pH by D_2EHPA (see Figures 8.10a, b); iron would then be stripped from the loaded organic by a HCl solution; the organic phase would then contact the leach solution (at a higher pH) to extract zinc; the zinc loaded organic would then be stripped by a sulfuric acid solution.

The procedure consisted of connecting the Reister testrack to provide a flow pattern as presented in Figure 5.7.: one stage of iron loading; one stage

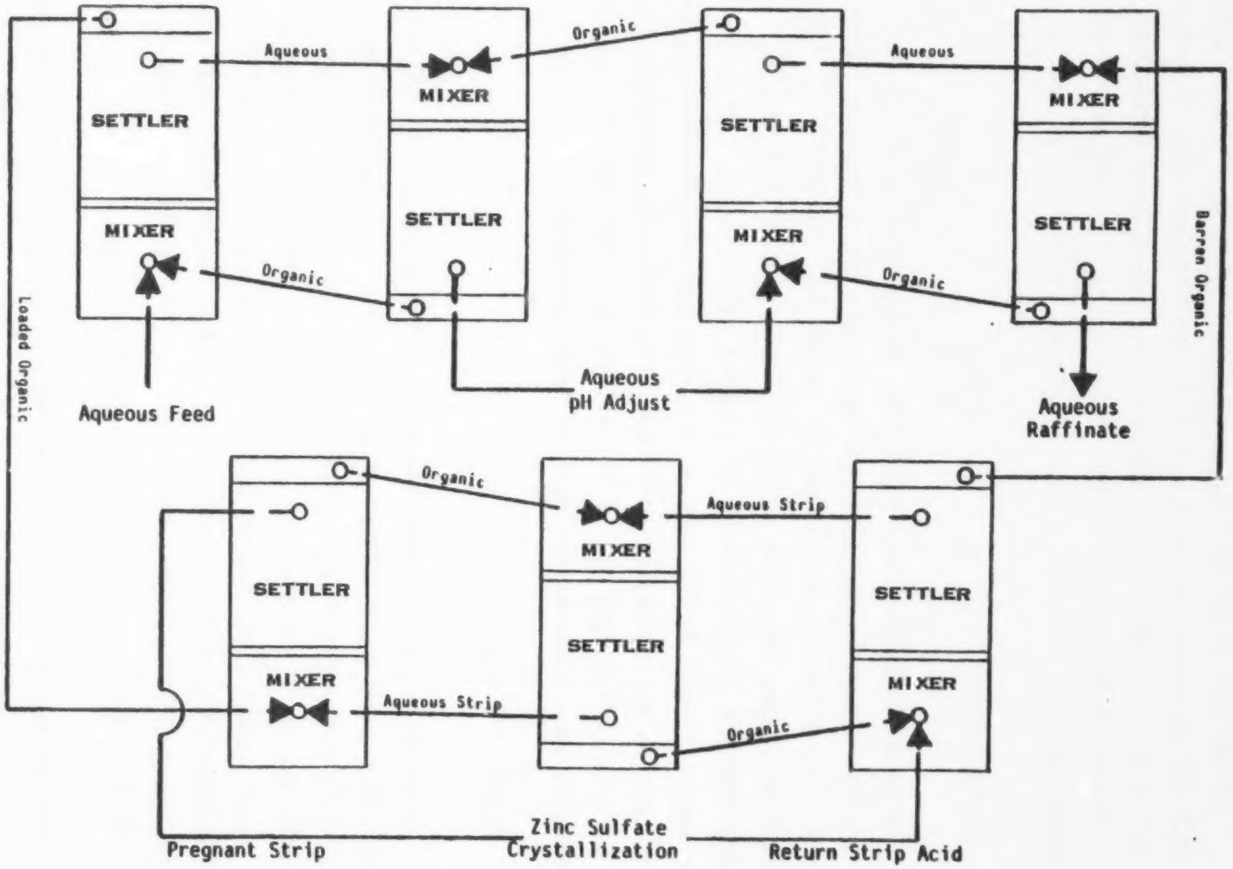

Aqueous
Organic
Aqueous
SETTLER
MIXER
Organic
MIXER
SETTLER
Organic
SETTLER
MIXER
Organic
MIXER
SETTLER
Barren Organic
Loaded Organic
Aqueous Feed
Aqueous
pH Adjust
Aqueous
Raffinate
Organic
Aqueous Strip
SETTLER
MIXER
MIXER
SETTLER
SETTLER
MIXER
Aqueous Strip
Organic
Pregnant Strip
Zinc Sulfate
Crystallization
Return Strip Acid

Figure 5.6. Zinc solvent extraction flow pattern.

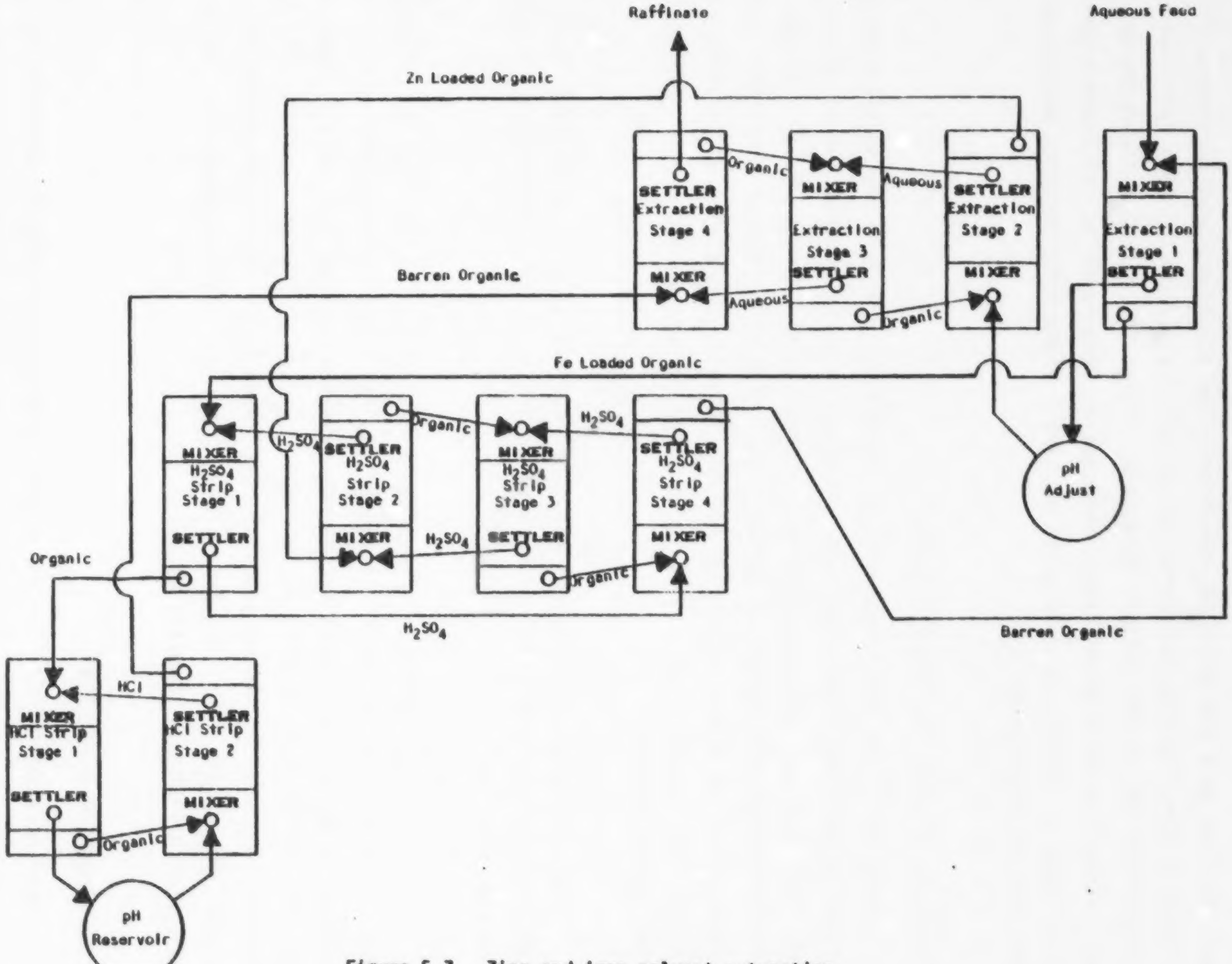

Raffinate
Aqueous Feed
Zn Loaded Organic
Organic
Aqueous
SETTLER Extraction Stage 4 MIXER
MIXER Extraction Stage 3 SETTLER
SETTLER Extraction Stage 2 MIXER
MIXER Extraction Stage 1 SETTLER
Barren Organic
Aqueous
Organic
Fe Loaded Organic
pH Adjust
MIXER H_2SO_4 Strip Stage 1 SETTLER
SETTLER H_2SO_4 Strip Stage 2 MIXER
MIXER H_2SO_4 Strip Stage 3 SETTLER
SETTLER H_2SO_4 Strip Stage 4 MIXER
H_2SO_4
Organic
H_2SO_4
H_2SO_4
Organic
H_2SO_4
Barren Organic
Organic
HCl
MIXER HCl Strip Stage 1 SETTLER
SETTLER HCl Strip Stage 2 MIXER
Organic
pH Reservoir

Figure 5.7. Zinc and iron solvent extraction.

of sulfuric acid stripping after iron loading for zinc removal (ferric ions are not stripped by a 200 gpl H_2SO_4 solution); two stages of iron stripping; three stages of zinc loading; and three stages of zinc stripping. The cells were loaded with the proper organic to aqueous ratio; the solution flowrates and cell interfaces were established; and samples were taken of raffinate after each stage of contact as a function of time. Phase interferences were observed for muck or crud formation.

5.2.2.3. Organic Degradation Testwork

Long term load strip testwork was conducted in a Bell engineering 600 cc, ten-stage continuous testrack. The testrack cells were connected to provide one stage (low pH) extraction of iron; three stages (higher pH) of zinc and iron extraction; one stage of sulfuric strip for zinc removal from the iron loaded (small amount of zinc also loaded) organic; two stages of sulfuric strip for the zinc loaded organic; and three stages of hydrochloric acid strip for iron loaded organic.

The purpose of the testwork was to expose the organic extractant to a long term, many cycle load-strip sequence to determine whether the extractant was degraded with use.

Potential degradation of the organic extractant was followed by closely monitoring the element concentration in the raffinate solution and by collecting organic samples after approximately every twenty liters of aqueous contact. The organic sample was stripped twice with 200 gpl sulfuric acid then exposed to a standard leach solution (two contacts). The effectiveness of the organic phase extractant was determined by its ability to remove zinc and iron selectively from the standard solution.

5.3. CHROMIUM OXIDATION

The oxidation of Cr^{+3} in the aqeuous phase was studied by exposure to chlorine gas (and other oxidizing agents) and by electrochemical oxidation.

5.3.1. Chromium Oxidation by Chlorine

5.3.1.1. Phase I Study

The oxidation of chromium by chlorine gas was studied first on a 100-500 cc scale; followed by 1.5-15 liter scale tests; then large scale tests at thirty liters and seventy-five liters. The procedure was to prepare a solution with appropriate chromium content (usually prepared by kettle leaching a sludge, removing the iron by jarosite precipitation, removing the copper by LIX-622 solvent extraction, removing the zinc by D_2EHPA solvent extraction); adjust pH; purge in chlorine to establish a desirable solution Eh; sample as a function of time to determine the extent of Cr^{+3} to C^{+6} oxidation.

Large scale testwork was performed in a 40-liter polypropylene vessel and in a 120-liter polypropylene vessel. (A schematic representation of the reaction system is presented in Figure 5.8). A chlorine lance was constructed from PVC and the sparge rate adjusted to maintain the solution Eh at approximately 1000 mv. The experimental results are presented in Section 8.9.1.1.

5.3.1.2. Phase II Study

Large scale testwork was continued during the Phase II study using an efficient chlorine gas-solution contactor system; a chlorinator. A chlorinator in its simplest design resembles an aspirator system. Liquid solution is pumped through a venturi. Pressure change is generated that aspirates chlorine through a side port. Turbulence is created in the solution by movement through chlorine gas. A schematic drawing of the chlorinator system is presented in Figure 5.9. The experimental results and discussion of results are presented in Section 6.36 and Appendix 8.9.1.1.2.

5.3.2. Electrochemical Oxidation

5.3.2.1. Phase I Study

Solution oxidation of chromium in an electrochemical reactor is depicted schematically in Figure 5.10. Only small scale oxidation studies were

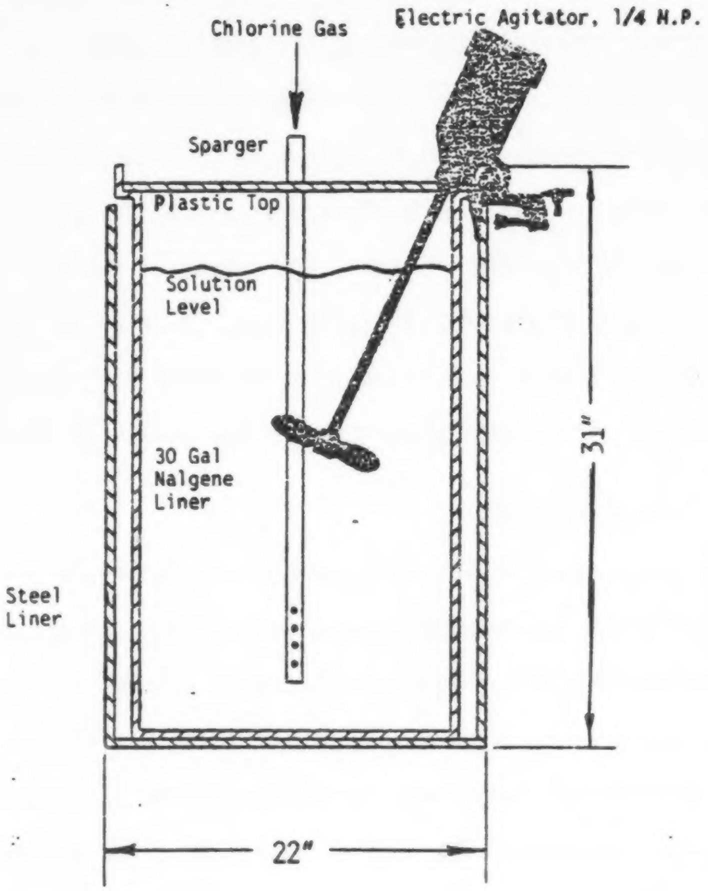

Chlorine Gas
Electric Agitator, 1/4 H.P.
Sparger
Plastic Top
Solution Level
30 Gal Nalgene Liner
Steel Liner
31"
22"

Figure 5.8. Chlorine oxidation reaction vessel (Cross section view).

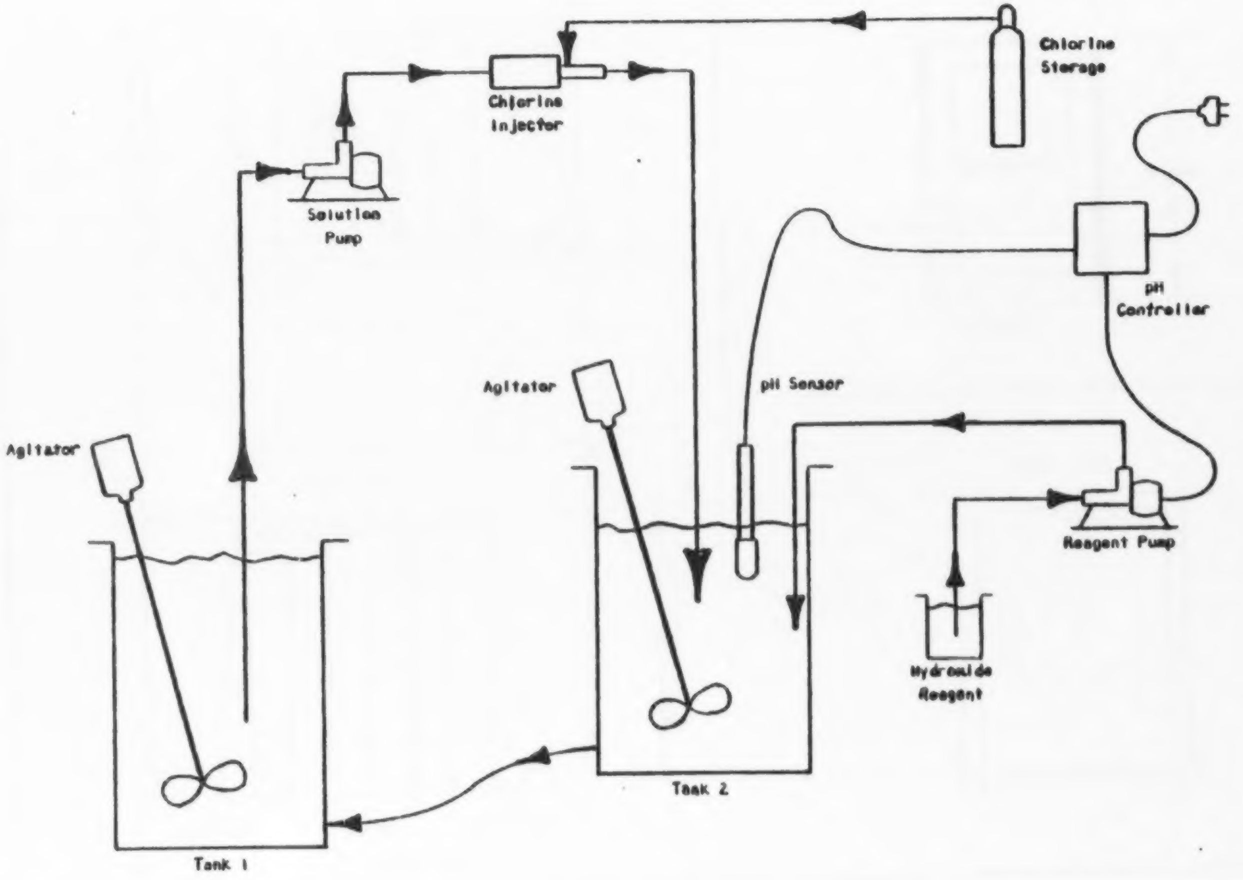

Chlorine Storage
Chlorine Injector
Solution Pump
pH Controller
pH Sensor
Agitator
Agitator
Reagent Pump
Hydroxide Reagent
Tank 1
Tank 2

Figure 5.9. Schematic drawing of the chlorinator system.

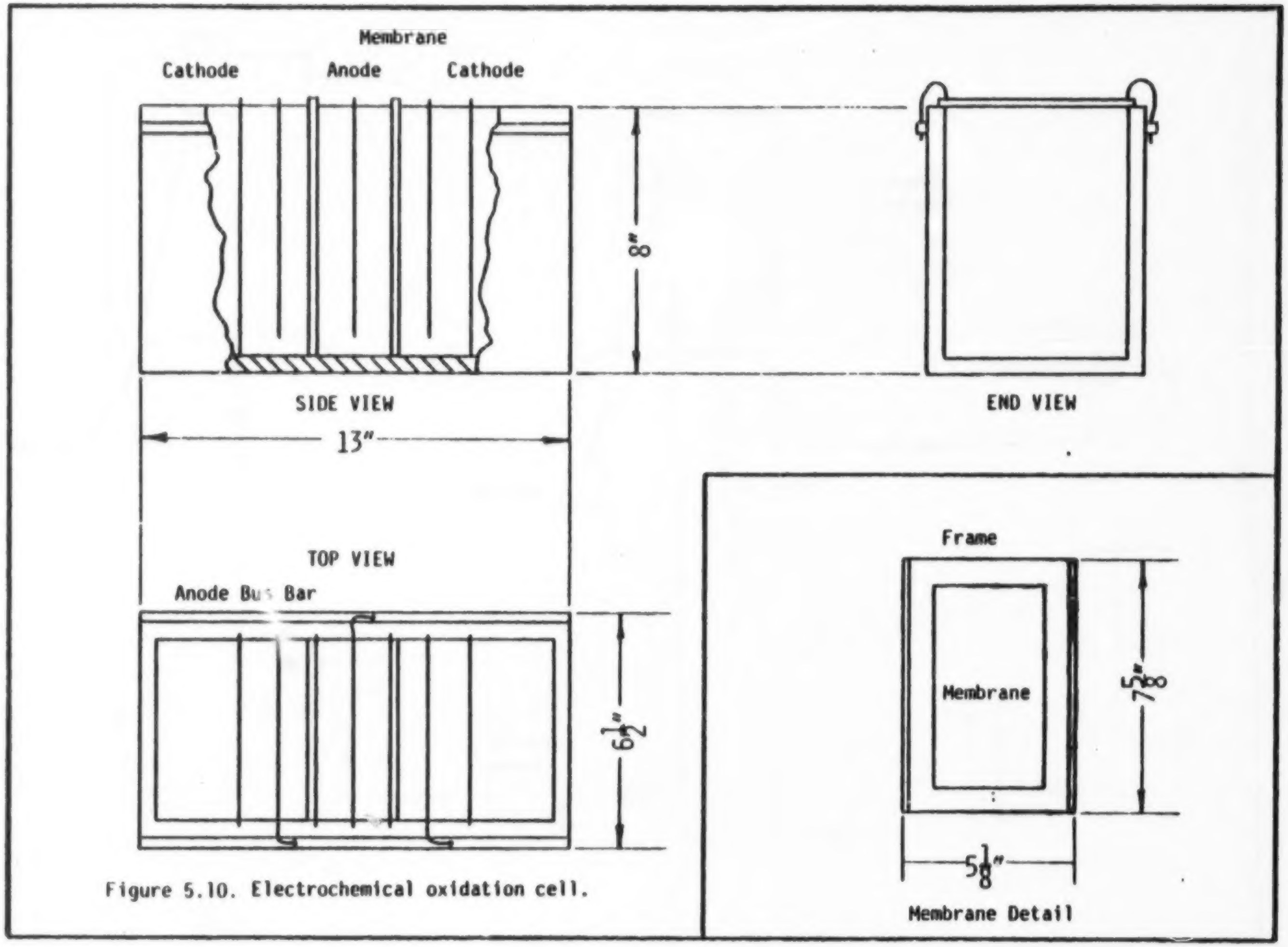

Membrane
Cathode
Anode
Cathode
8"
SIDE VIEW
13"
END VIEW
TOP VIEW
Anode Bus Bar
6½"
Frame
Membrane
7⅝"
5⅛"
Membrane Detail

Figure 5.10. Electrochemical oxidation cell.

conducted in the Phase I study. The results were very encouraging and a large scale reactor was included in the second phase study. Two small scale studies were performed; a series of batch oxidations and a continuous flow oxidation study. A summary of the experimental results is presented in Section 8.9.1.2.

The batch tests were performed on zinc raffinate prepared during the sequential series five testwork. The solution was, therefore, relatively free of Fe, Cu, and Zn. The solution contained a mixture of chromium and nickel. This solution was used to fill the anode chamber (approximately one liter) and a 180 gpl H_2SO_4 solution was used to fill the cathode chambers. The desired cell voltage and current density were established and the oxidation allowed to proceed for a designated time. Samples were taken as a function of time and analyzed for all metal values and for Cr^{+3}/Cr^{+6} content.

The continuous test was conducted on the same zinc raffinate solution. The anode chamber was filled with zinc raffinate partially oxidized previously in the batch tests (69% oxidized chromium). The two cathode chambers were filled with 180 gpl H_2SO_4. Unoxidized zinc raffinate was fed continuously into the anode chamber at 3-5 cc/min. and a similar volume was withdrawn. The exit stream was sampled as a function of time.

5.3.2.2. Phase II Study

An electrolytic cell was constructed of 3/8 in. acrylic sheet material. The cell dimensions were: 18 in. length, 12 in. width, 12 in. depth. Overflow weirs were provided along the two sides of the cell. The overflow solution was collected at the ends of the cell and was recirculated to the bottom of the cell. The base of the cell was fit with a false bottom in the shape of an inverted acrylic pan one-inch high. Solution distribution holes (1/32 in. diameter) were placed on all four sides of the pan at 1/4 in. intervals to insure that the recirculating solution was evenly distributed in its flow back into the chamber.

A second cell was constructed of 1/4 in. acrylic sheet; 14 in. length, 6 in. width, and 12 in. depth. The two long sides were cut and fit with a 11 in.

by 10 in. Nafion 423 diaphragm. The diaphragms were secured in place by plastic flanges. A cross pipe was drilled with small holes and placed along the length of each Nafion diaphragm. This arrangement allowed air to be blown upward across the face of the diaphragm. The two chambers are depicted schematically in Figures 5.11 and 5.12.

The electrochemical oxidation cell was formed by setting the smaller chamber inside the larger chamber on the false bottom. The inner chamber is the anolyte cell where oxidation occurs. The outer chamber is the catholyte cell where reduction occurs. Anolyte solution containing the Cr^{+3} and Ni^{+2} ions is prevented from intermixing with the catholyte solution containing sulfuric acid by the walls and the Nafion diaphragms. Busbars for current flow were made from 3/4 in. copper tubing. Current was supplied to the busbars by a 100 amp DC power supply (Lambda Model LES-F).

Electrode material was lead. Electrodes were 1/4 in. sheets by 12 in. by 4 in. (both cathodes and anodes). Later in the study special high surface area anodes were constructed and investigated. These anodes were constructed using a 1/8 in. perforated lead sheet. A 12 in. by 6 in. section of the perforated lead sheet was laid down and layered with plumber's lead wool then overlapped with a section of perforated lead sheet. The sides were folded over and crimped to form a structurally strong anode.

Initial static tests (anolyte was not continuously fed into the anode chamber) were performed using the lead sheet electrodes with an anode:diaphragm:cathode ratio of 1:1:1. The applied voltage was 3.5 v. The initial current density (c.d.) was 8 amp/ft^2. The c.d. increased to 12 amp/ft^2 over a 24 hour period.

Anolyte solutions were sampled and analyzed for total chromium, hexavalent chromium, and nickel. The hexavalent (oxidized form of chromium) was determined by exposing an aliquot of the anolyte to an equal volume of Rohm and Haas anionic exchange resin IR-900. The resin-anolyte mixture was shaken for five minutes, then the solution was recovered and analyzed for chromium content

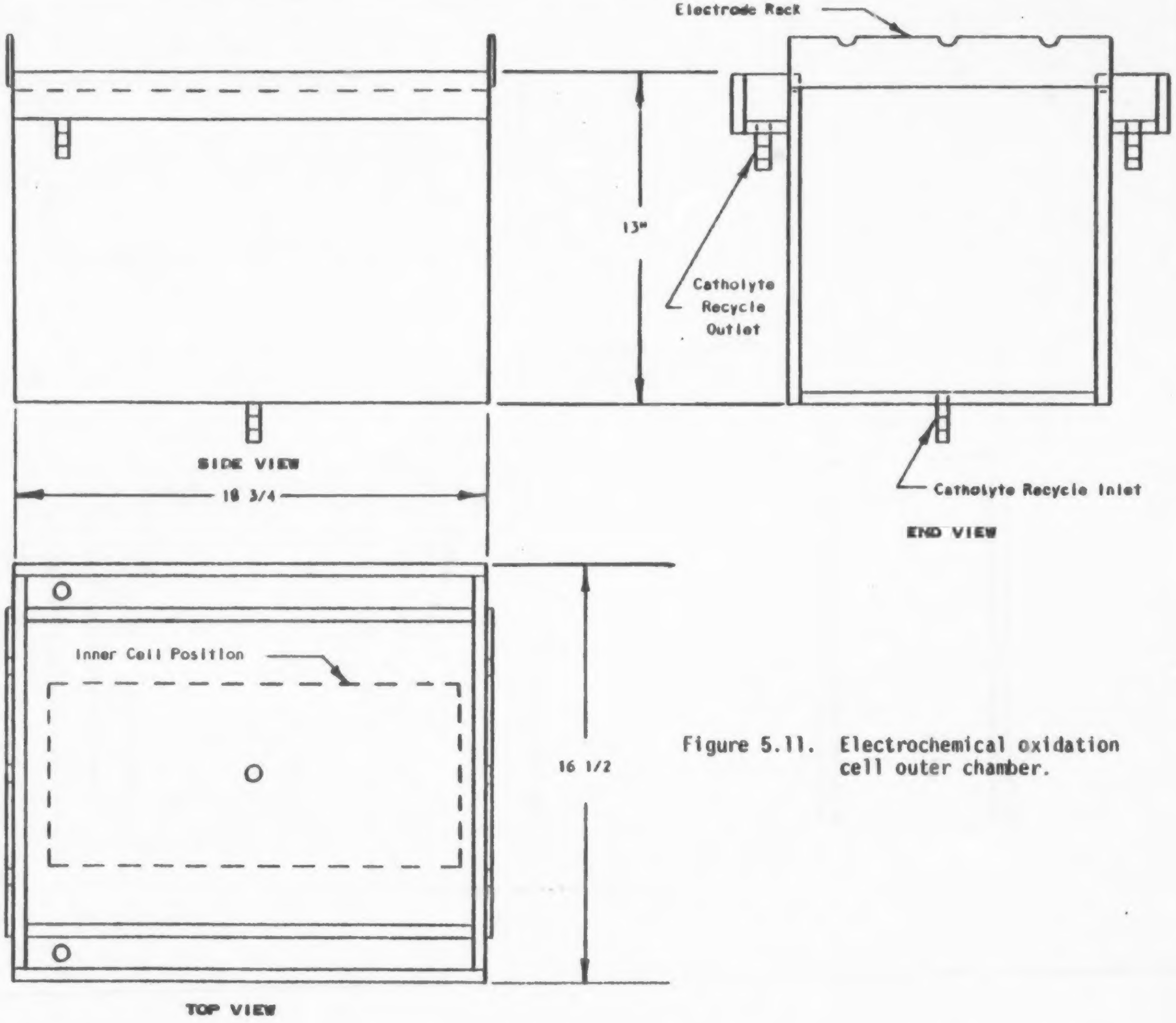

Electrode Rack
13"
Catholyte Recycle Outlet
SIDE VIEW
18 3/4
Catholyte Recycle Inlet
END VIEW
Inner Cell Position
16 1/2
TOP VIEW

Figure 5.11. Electrochemical oxidation cell outer chamber.

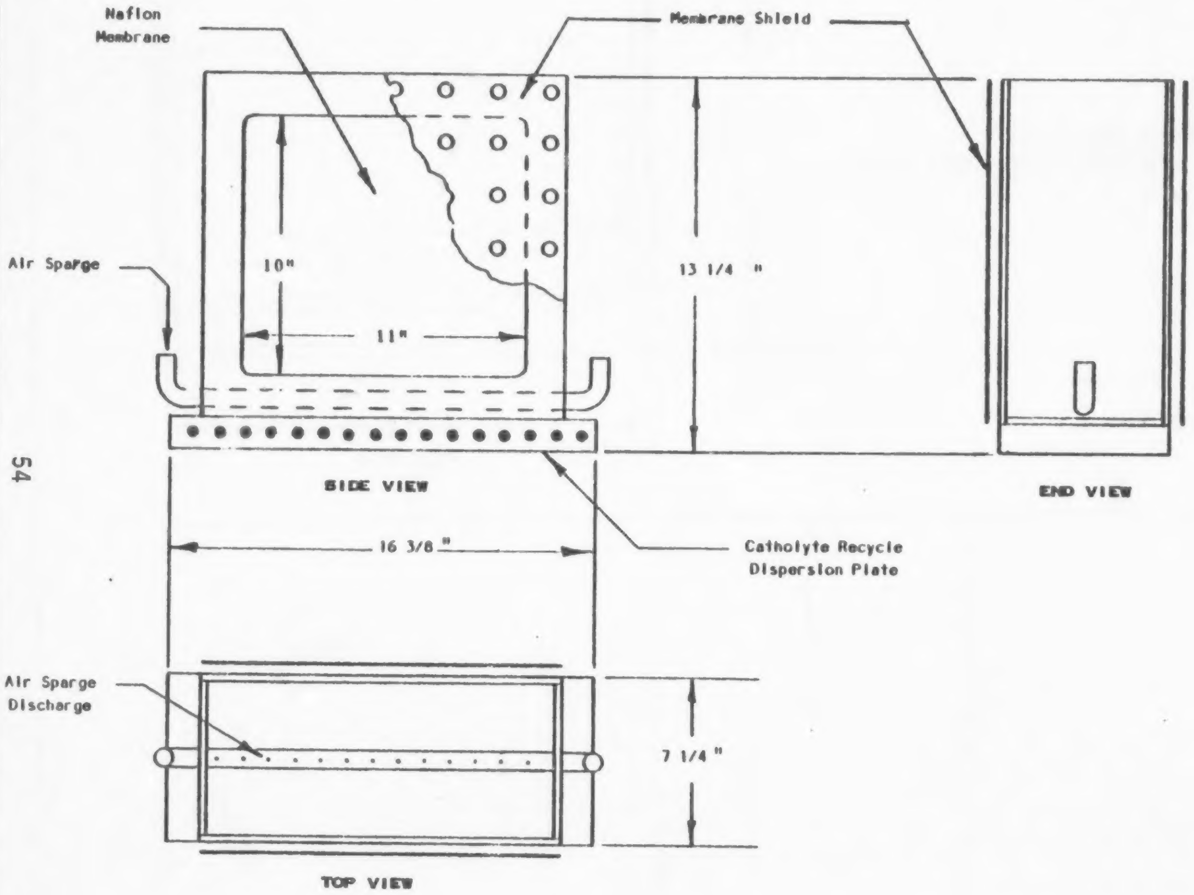

Naflon
Membrane
Membrane Shield
Air Sparge
10"
11"
13 1/4 "
SIDE VIEW
END VIEW
16 3/8 "
Catholyte Recycle
Dispersion Plate
Air Sparge
Discharge
7 1/4 "
TOP VIEW

Figure 5.12. Electrochemical oxidation cell inner chamber.

(only Cr^{+3} remained, the Cr^{+6} as $Cr_2O_7^{=}$ ions were removed by the exchange resin). The difference between the total chromium in the original sample and the chromium analyzed in the ion exchange resin treated solution was taken as the hexavalent chromium content. A standard solution of chromic acid containing 20 gpl Cr was prepared. An aliquot of this solution was treated similar to a test solution. Hexavalent chromium extraction by the resin in five replicate samples showed 98.6 ± 1.5 percent removal by the ion exchange resin.

Catholyte solutions were analyzed for total chromium and nickel. All solution analyses were performed using a Perkin-Elmer 303 atomic absorption spectrophotometer using a nitrous oxide-acetylene flame.

The results and discussion are presented in Section 6.3.6. and Appendix 8.9.1.2.

5.4. CHROMIUM PRECIPITATION

The oxidation of chromium (Section 5.3.) resulted in a leach solution containing only chromium, as $Cr_2O_7^{-2}$ or $HCrO_4^{-1}$, and Ni^{+2}. The oxidized chromium can be separated from the nickel cations by precipitation as lead chromate. The lead chromate precipitation is a way of removing the chromium selectively from the nickel and it also provides a means of concentrating the chromium, i.e., the separated lead chromate solid phase can be releached to form a high concentration chromic acid and solid lead sulfate. The lead sulfate then can be recycled to the oxidized leach solution to precipitate more chromium.

The experimental procedure used to consider the precipitation of chromium consisted of small beaker tests to observe the effect of pH, time, and amount of $PbSO_4$ on the recovery of chromium from solution. These tests were followed by large scale precipitation experiments in an agitated vessel. The large scale test procedure consisted of feeding a predetermined amount of lead sulfate into 45 liters of a leach solution previously sequentially treated for Fe, Cu, and Zn removal; agitating the solution to suspend the solids; reacting for a designated time; sampling the aqueous phase as a function of time so that the degree of chromium removal could be determined; maintaining the pH in the range 3.5-4.5; terminating the agitation to allow the solids to settle (15-30 minutes); decanting most of the solution from the solids; and recovering the $PbSO_4$-$PbCrO_4$ solids by filtration; redissolution of the lead chromate in the solids in a sulfuric acid solution to determine the ability to concentrate the chromium and to observe the contamination of other metal ions in the resulting chromic acid. The results and discussion of results are presented in Section 6.3.7 and Appendix 8.10.1.

5.5. NICKEL RECOVERY

Nickel is the last metal ion to be removed from solution. Its concentration in solution is usually in the range of 2 to 6 grams per liter. Therefore, it must be concentrated. Two major means of concentration were investigated, i.e., precipitation as nickel sulfide and solvent extraction.

5.5.1. Sulfide Precipitation

Sulfide precipitation was investigated by small scale testwork utilizing a design matrix to establish the important experimental variables. Tests were conducted in small beakers to establish the influence of pH, time, and Na_2S concentration. The small scale testwork was followed by a large batch test on 42 liters of leach solution (pretreated for Fe, Cu, Zn, and Cr removal).

The large scale test procedure consisted of: feeding a solution of Na_2S slowly into the reaction vessel; maintaining the solution pH in the range 4-4.5; sampling as a function of time; agitating the slurry to keep the precipitated nickel sulfide suspended in the solution phase; terminating the agitation and filtering the solids from the solution. The results and discussion of results are presented in Section 6.3.8 and Appendix 8.11.1.

5.2.2. Solvent Extraction of Nickel

Solvent extraction of nickel is not commercially practiced (except in ammoniacal solutions). Therefore, only preliminary small scale tests were

Conducted to investigate potential solvent extraction concentration of nickel. All of the testwork was performed in small (125-250 cc) separatory funnels. The procedure used was the same as described for copper extraction in Section 5.2.1.1. The results and discussion of results are presented in Section 8.11.2.

SECTION 6

RESULTS AND DISCUSSION

6.1. LARGE SCALE SEQUENTIAL TEST MASS BALANCE (HIGH IRON)

A flowsheet summarizing large scale sequential experimental studies is presented in Figure 6.1. Included are mass balances for Cu, Fe, Zn, Cr, Ni, Cd, Al, and Ca. A summary of the distribution of each element into the various products is presented in Tables 6.1 and 6.2. The metal content of each solid product is presented in Table 6.3. The element distributions presented in Figure 6.1 and Tables 6.1 through 6.3 are based on calculated values for 100 pounds of sludge and are, therefore, hypothetical numbers. The distributions are, however, based on data generated in the large scale sequential testwork presented in Section 8.13.

The throw-away product in the process is the leach residue-jarosite solid mixture; i.e., there are about 15,000 grams (33 pounds) of solids in the starting 45,400 grams (100 pounds) of sludge; from the leach of this solid material 4,800 grams of leach residue remain and 6,800 grams of jarosite are produced. A large fraction of the iron (>95%) is rejected to the solid. Some metal values are also lost to the solids; i.e., 10% copper, 6% Zn, 18% Cr, and 6% Ni. The copper loss is higher in the large scale testwork than noted in the small scale testwork; nickel and zinc are similar to other testwork; and chromium loss is quite variable but usually falls within the range of about 15 to 25 percent.

The reason for the apparently high copper and chromium loss during the jarosite precipitation process is related to the presence of phosphorus (note the sludges in the Phase I study contained 2-4% phosphorus, Table 4.1). The jarosite conditions are ideal for the partial deposition of copper and chromium as phosphates; see Figure 6.2. The equilibrium chromium content (at 80°C) is

Figure 6.1 Treatment of 45.4 kg (100 lbs.) of high iron metal hydroxide sludge per day: element distribution.

45.4 kg (100 pounds)/day

	Volume or Mass		Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
			Concentration (kg/day or %)							
1. Sludge (33% solids)	: 15.0 kg solids	kg	2.56	0.87	1.24	0.91	0.34	0.01	0.42	0.30
	30.4 kg solution	%	17.1	5.8	8.3	6.1	2.3	0.10	2.8	2.0
2. Recycle Solids (35% solids):	0.34 kg solids	kg	0.13	0.00	<D.L.	0.11	0.00	<D.L.	0.03	<D.L.
	0.65 kg solution	%	5.8	0.0	<D.L.	32.3	0.2	<D.L.	8.8	<D.L.
3. Recycle Solution	: 188.0 l	kg	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.	<D.L.
4. H_2SO_4 Acid	: 10.2 l (41.6 lbs.)									

↓

Acid Leach
- 40-60°C
- 0.5 hr.
- pH = 0.5-1.5

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
Extractions (%):	92.0	93.7	95.1	96.5	95.9	93.0	96.9	15.0

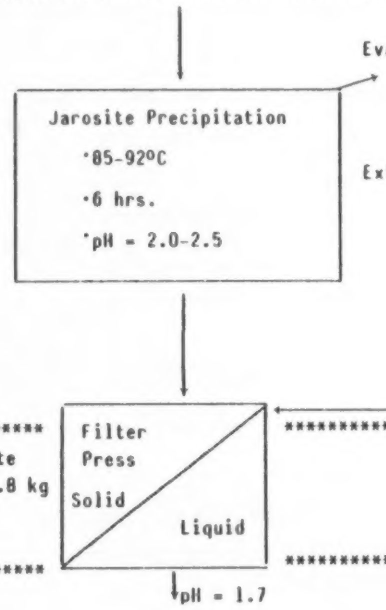
↓ pH = 1.0-1.5

	Volume or Mass		Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
			Concentration (kg/day or gpl)							
5. Leach Solution	: 229 l	gpl	10.29	3.59	5.17	3.84	1.42	0.06	1.77	0.20
		kg	2.36	0.82	1.18	0.88	0.32	0.01	0.40	0.04

Figure 6.1. Continued

	Volume or Mass		Concentration (kg/day or %)							
			Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
6. Residue Solids (not separated, i.e., subsequent jarosite precipitation performed in presence of leach residue)	: 4.8 kg (dry basis)	kg	0.21	0.06	0.06	0.03	0.01	0.00	0.01	0.25
		%	4.3	1.2	1.3	0.7	0.3	0.0	0.3	5.3
7. KOH Solution (500 gpl)	: 10.0 l									
8. H_2O_2 (30%)	: 2.5 l									

****


Jarosite Precipitation
·85-92°C
·6 hrs.
·pH = 2.0-2.5
Filter Press
Solid
Liquid
pH = 1.7

Evaporative Solution Loss: 24 l

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
Extractions (%):	97.0	2.7	2.0	15.0	3.6	6.2	44.5	0.0

[NOTE: Chromium loss would be much less if the jarosite solids are releached with H_2SO_4 at a pH of < 0.5]

13 l wash water

****

9. Leach residue - jarosite Solid (65% solid): 17.8 kg (11.6 kg solids, 6.2 kg solution)

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
kg	2.50	0.08	0.08	0.16	0.02	0.00	0.19	0.25.
%	21.6	0.7	0.7	1.4	0.2	0.0	1.6	2.2

****

Figure 6.1. Continued

10. Filtrate : 224 l

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
	Concentration (kg/day or gpl)							
gpl	0.31	3.51	5.09	3.30	1.36	0.00	0.98	0.18
kg	0.07	0.80	1.16	0.75	0.31	0.00	0.22	0.04

Solvent Extraction of Copper
- Initial pH = 1.7
- Temp. = 40-50^{0}C
- Two-stage extraction, O/A=1
- Two-stage strip, O/A=1, 180 gpl H_2SO_4
- 15 v/o LIX-622, 85 v/o KERMAC 470B
- 250 cc/min. each phase

Extraction Efficiency: Stage 1 - 96.8% Cu
Stage 2 (pH = 1.5) - 95.3% Cu

pH = 1.4

11. Copper may be electrowon (0.80 kg)
or
crystallized as $CuSO_4 \cdot 5H_2O$ (3.15 kg)

12. Raffinate : 224 l

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
	Concentration							
gpl	0.31 (90% Fe^{+++})	0.005	5.09	3.30	1.36	0.00	0.98	0.18
kg	0.07	<0.01	1.16	0.75	0.31	0.00	0.22	0.04

13. NaOH (400 gpl): 1 liter

Figure 6.1. Continued

Solvent Extraction of Zinc
- Initial pH = 2.5
- Temp. = 40-50°
- Four stages of extraction, pH adjusted back to 2.5 after second stage, O/A=1
- Three stages of strip (200 gpl H_2SO_4), O/A=1
- 40 v/o DEHPA, 60 v/o KERMAC 470B

Stage:	1	2
	70.0% Zn	50.0% Zn
	30.0% Al	20.0% Al
	50.0% Ca	20.0% Ca
	50.0% Fe	20.0% Fe

Stage:	3	4
	70.0% Zn	50.0% Zn
	30.0% Al	20.0% Al
	50.0% Ca	20.0% Ca
	50.0% Fe	20.0% Fe

Strip Efficiency each stage : 85.0% Zn
50.0% Al
100.0% Ca
0.0% Fe

****

14. Zinc may be crystallized as $ZnSO_4 \cdot 7H_2O$

Composition of solution from which Zn is crystallized:

	Zn	Al	Ca	Fe	Cd
kg	1.14	0.15	0.03	0.00	0.00

↑ (ppt. as gypsum)

****

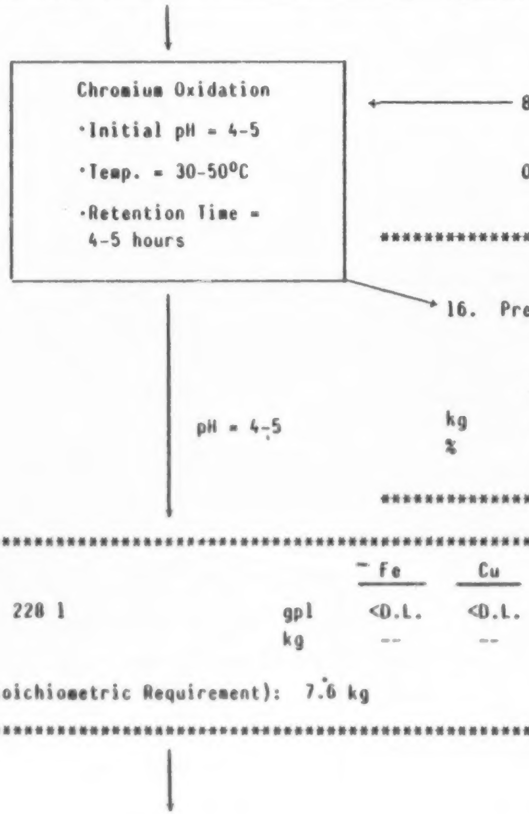
pH = 1.3

****

		Composition							
		Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
15. Raffinate: 224 l	gpl	0.07	0.00	0.11	3.30	1.36	0.00	0.27	0.03
	kg	0.02	0.00	0.02	0.75	0.31	0.00	0.07	0.01

****

Figure 6.1. Continued



Chromium Oxidation
- Initial pH = 4-5
- Temp. = 30-50°C
- Retention Time = 4-5 hours

8 liters 500 gpl NaOH

Oxidation Efficiency: 85%

pH = 4-5

****

16. Precipitate (35% solids): .34 kg solids
0.65 kg solution

	Fe	Cu	Zn	Cr	Ni	Cd	Al
kg	0.02	--	--	0.11	--	--	0.03
%	5.8	--	--	32.3	--	--	8.8

****

****

17. Oxidized Solution: 228 l

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Cd
gpl	<D.L.	<D.L.	0.11	2.81	1.36	<D.L.	0.13	0.03
kg	--	--	0.02	0.64	0.32	--	0.03	<0.00

18. Lead Sulfate (2X Stoichiometric Requirement): 7.6 kg

****

Figure 6.1. Continued

Chromium Precipitation

- Temp.: Ambient
- Time: 0.5 hr.
- 2X Stoichiometric Requirement of $PbSO_4$
- Initial pH = 3.5-4

0.6 l 500 gpl NaOH

Wash 2X Entrapped Solution: 5.2 l

pH = 3.5-4

****

19. $PbCrO_4$-$PbSO_4$ (70% solids): 6.0 kg $PbSO_4$-$PbCrO_4$
2.6 kg solution

	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
kg	0.00	--	--	0.64	--	--	0.03	--
%	0.0	--	--	11.0	00	00	0.5	--

****

****

20. Solution: 230 l

	Concentration							
	Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
gpl	<D.L.	<D.L.	0.09	0.008	1.40	--	--	0.03
kg	--	--	0.02	<0.00	0.32	--	--	<0.00

21. Na_2S Solution (325 gpl): 6 l

****

Figure 6.1. Continued

Nickel Precipitation

- Temp. = 25-35°C
- Time = 0.5 hr
- 2X Stoichiometric Requirement of Na_2S (not optimized)
- Initial pH = 3-4

0.5 l 400 gpl H_2SO_4

22. Sulfide Precipitate (35% solids): 0.5 kg solids
1.4 kg solution

	Ni	Cr	Zn	Al
kg	0.32	<0.00	0.02	<0.00
%	64.0	--	4.0	--

PH = 3-4

23. Recycle Solution (to leach and to water makeup): 231 l

	Concentration						
	Fe	Cu	Zn	Cr	Ni	Cd	Al
gpl	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.

To Recycle

TABLE 6.1. TREATMENT OF METAL HYDROXIDE SLUDGE: ELEMENT DISTRIBUTION SUMMARY

Input or Product (see Figure 6.1)	Mass (kg)	Volume (l)	Distribution (kg/day)							
			Fe	Cu	Zn	Cr	Ni	Cd	Al	Ca
Stream No.										
1. Sludge	15.0-solids	30.4 kg-solution	2.56	0.87	1.24	0.91	0.34	0.01	0.42	0.30
2. Recycle Solids	0.34-solids	0.65 kg-solution	0.13	0.00	<D.L.	0.11	0.00	<D.L.	0.03	<D.L.
3. Recycle Solution		188.0 l	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.	<D.L.
4. H_2SO_4 Acid		10.2 l								
5 Leach Solution		229.0 l	2.36	0.82	1.18	0.88	0.32	0.01	0.40	0.04
6. Residue Solids	4.8 kg		0.21	0.06	0.06	0.03	0.01	0.00	0.01	0.26
7. KOH (500 gpl)		10.0 l								
8. H_2O_2 (30%)		2.5 l								
9. Residue Solids-Jarosite	11.6-solids	6.2 kg-solution	2.50	0.08	0.08	0.16	0.02	0.00	0.19	0.26
10. Filtrate		224.0 l	0.07	0.80	1.16	0.75	0.31	0.00	0.22	0.04
11. Copper Strip Circuit		7.5 l aqueous 7.5 l organic	----	0.80	0.00	0.00	0.00	0.00	0.00	0.00
12. Cu Raffinate		224.0 l	0.07	<0.01	1.16	0.75	0.31	0.00	0.22	0.04
13. NaOH (400 gpl)		1.0 l								
14. Zinc Strip Circuit		11.5 l Aqueous 11.5 l Organic	0.05	0.00	1.14	0.00	0.00	0.00	0.15	0.03
15. Zinc Raffinate		224.0 l	0.02	0.00	0.02	0.75	0.31	0.00	0.07	0.01
16. Precipitate (same as #2)	0.34 -solids	0.65 kg-solution	0.02	0.00	<D.L.	0.11	0.00	<D.L.	0.03	<D.L.
17. Oxidized Solution		228.0 l	0.00	0.00	0.02	0.64	0.32	0.00	0.03	0.00
18. Lead Sulfate	7.6 kg									
19. $PbCrO_4$-$PbSO_4$	6.0-solid	2.6 kg-solution	0.00	0.00	0.00	0.64	0.00	0.00	0.03	0.00
20. Solution		230.0 l	0.00	0.00	0.02	0.00	0.32	0.00	0.00	0.00
21. Na_2S Solution (325 gpl)		6.0 l								
22. Sulfide Precipitate	0.5-solid	1.3 kg-solution	0.00	0.00	0.02	0.00	0.32	0.00	0.00	0.00
23. Recycle Final Soln.		23.5 l	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.	<D.L.

TABLE 6.2. TREATMENT OF METAL HYDROXIDE SLUDGE: DISTRIBUTION TO SPECIFIC PRODUCTS

Distribution To Specific Product	Distribution (%)						
	Fe	Cu	Zn	Cr	Ni	Al	Ca
Leach Residue-Jarosite	97.6	9.2	6.4	17.6	5.9	42.2	86.6
Copper SX Circuit	0.0	92.0	0.0	0.0	0.0	0.0	0.0
Zinc SX Circuit	2.0	0.0	91.9	0.0	0.0	33.3	10.0
Chromium Slurry Oxidation Solid (Recycled to Leach)	0.8	0.0	0.0	12.1	0.0	7.1	0.0
Lead Chromate-Lead Sulfate	0.0	0.0	0.0	70.3	0.0	6.7	0.0
Sulfide Precipitate	0.0	0.0	1.6	0.0	94.1	0.0	0.0

Notes:
- Distribution balance based on flowsheet Figure 6.1.
- Detailed experimental results for large scale sequential testwork presented in Section 8.13.

TABLE 6.3. TREATMENT OF METAL HYDROXIDE SLUDGE: ELEMENTAL CONTENT IN SOLID PRODUCTS

Product	Elemental Content (%)						
	Fe	Cu	Zn	Cr	Ni	Al	Ca
Starting Sludge (Solids)	17.1	5.8	5.3	6.1	2.3	2.8	2.0
Leach Residue	4.4	1.2	1.2	0.6	0.2	0.2	5.4
Jarosite	33.7	0.3	0.3	1.9	0.1	2.6	3.8
Lead Chromate-Lead Sulfate (27.9% $PbSO_4$, 68.3% $PbCrO_4$, 1.5% $Al(OH)_3$.	0.0	0.0	0.0	11.0	0.0	0.5	0.0
Nickel Sulfide	0.0	0.0	0.4	0.0	64.0	0.0	0.0

Notes:
- Based on flowsheet Figure 6.1.
- Detailed experimental results for large scale sequential testwork presented in Section 8.13.

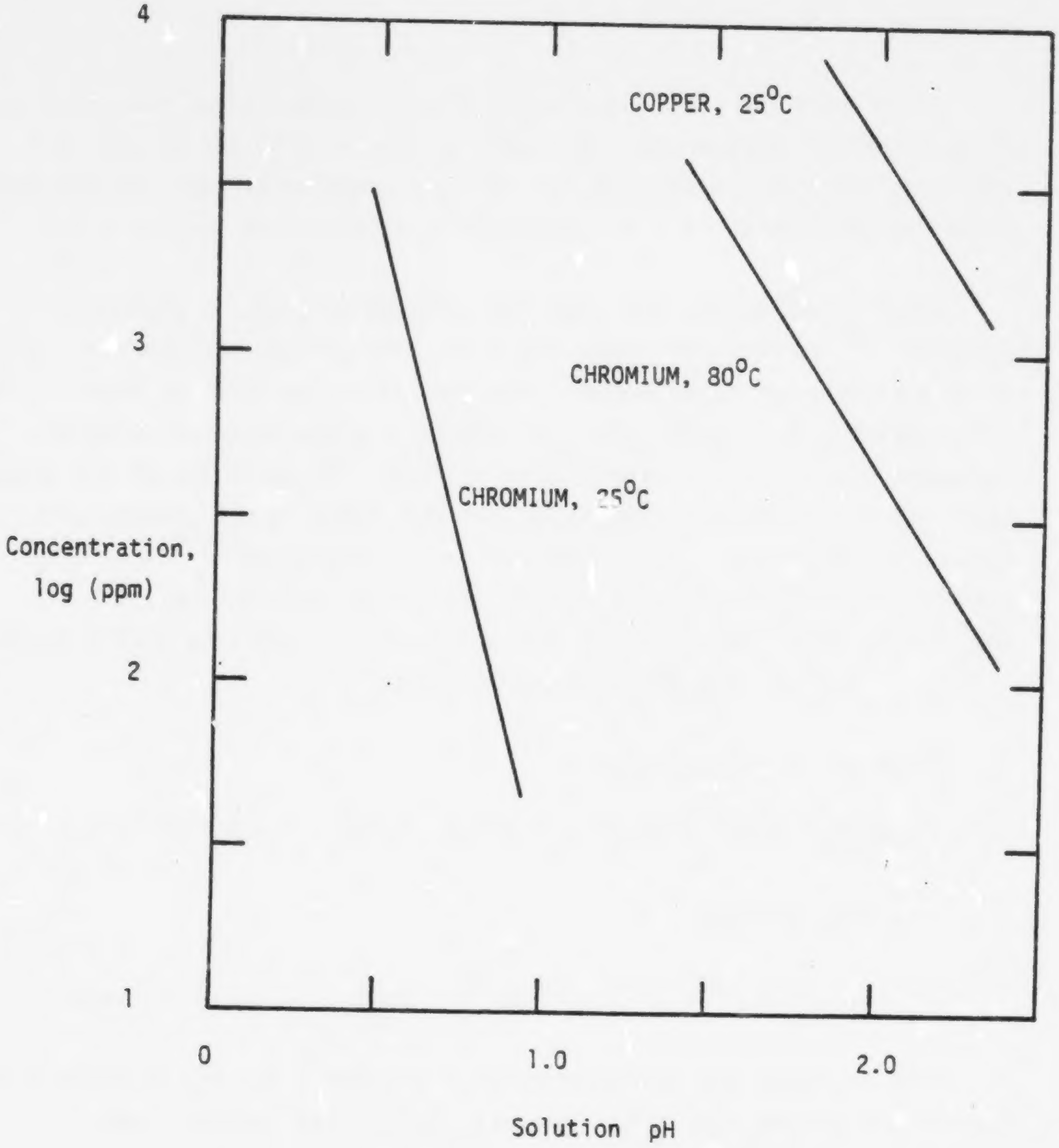


Figure 6.2. Solubility of chromium and copper phosphates.

about 0.5 gpl at pH of 2.0. The effect of phosphate precipitation is not considered a deterent because the jarosite (once formed it does not readily redissolve in acid solutions) can be releached to redissolve the chromium phosphate and copper phosphate.

If an operating plant has phosphorus containing sludges then an acid releach (pH and temperature controlled) of the jarosite may be desirable. The resulting leach stream could be fed into the solution stream from the jarosite filtering unit operation. This approach is discussed in Section 6.3.2.

Other investigators have reported chromium contents in potassium jarosite(1,2) to be in the range 0.6-1.6%. The present results show 1.9% Cr. It is presently not clear whether this loss is a true chromium substitution for iron to form $K(Fe,Cr)_3(OH)_6(SO_4)_2$ or whether a coprecipitated chromium phosphate phase forms on the jarosite surface. The condition of the sequential tests was very oxidizing. This also has been noted in the present work to enhance chromium loss. It is reported in the literature(3,4) that $CrO_4^=$ may substitute completely for $SO_4^=$ in the jarosite structure, i.e., a $KFe_3(CrO_4)_2(OH)_6$ compound forms. Therefore, under highly oxidizing conditions the following reactions are expected to occur:

Chromium is oxidized slowly,

$$3H_2O_2 + 2Cr^{+3} + 2H_2O \quad = \quad 2HCrO^-_4 + 8H^+ \qquad \varepsilon^o = 0.6 \text{ volts}$$

Iron also oxidizes

$$H_2O_2 + 2Fe^{+2} + 2H^+ \quad = \quad 2Fe^{+3} + 2H_2O \qquad \varepsilon^o = 1.0 \text{ volts}$$

Both reactions are thermodynamically feasible. As long as there is any ferrous ion present the $HCrO_4^-$ ions will oxidize the ferrous ions:

$$HCrO_4^- + 3Fe^{+2} + 7H^+ \quad = \quad 3Fe^{+3} + Cr^{+3} + 4H_2O \qquad \varepsilon^o = 0.4 \text{ volts}$$

When the iron has all been oxidized, $HCrO_4^-$ (present at all pH levels if chromium content is less than ≈ 1 gpl(5)), then should form. This oxidized chromium is, therefore, available for reaction to form the jarosite. Therefore, proper solution conditions must be chosen to minimize chromium loss, i.e., the addition of a minimum amount of oxidizing agent is required (sufficient to oxidize the iron but not the chromium). Also significantly less loss of chromium can be expected in those systems that are relatively low in iron content, e.g., if 0.6-1.6% Cr^{+3} is incorporated in the jarosite precipitate(2) then if the iron content in a solution is 1 gpl (and the chromium level remains at 3.8 gpl as illustrated in Figure 6.1.) instead of ten grams per liter the loss of chromium to the solid would drop to the range 0.1 to 0.4% or less. This conclusion needs further testwork for verification but kettle test results support the conclusion. Further discussion of impurity incorporation in precipitated jarosite is included in Appendix Section 8.3.1.

A list of summary comments for each large scale unit operation is presented below. A detailed presentation and discussion of all large and small scale testwork are presented in the following section, 6.3, and in Appendices 8.2-8.16.

- The sulfuric acid leach operation is effective in redissolving the metal values. The dissolution is rapid and without control problems. The leach is carried out in a single 270 liter vessel. The conditions required are well characterized, and rather mild, i.e., one-half hour, 40-50°C, sludge/liquid ratio of 0.8, acid content to control pH in the range 0.5-1.5, and agitation sufficient to suspend the particulate in the solution phase.

  The sludge dissolution is essentially complete in less than one-half hour. Therefore, the leach operation is not the controlling step in the overall treatment sequence. The leach unit operation is capable of treating over a ton of sludge per eight hour day. The filterability of the leach residue product is difficult. The filterability of a mixed leach residue-jarosite product is rapid and effective. Therefore, in most testwork the jarosite precipitation process was performed in-situ with the leach residue solids.

- The iron removal unit operation is via the precipitation of potassium jarosite. The precipitation process requires elevated temperatures and relatively long reaction times. Two hundred liters of leach solution slurry can be treated in six-eight hours.

The jarosite process allows iron to be removed from an acid solution. The product is a crystalline compound that has excellent settling and filtering properties. The iron removal process has been demonstrated on high iron sludge materials, i.e., 15-20% iron in the starting sludge solids. This means that for these particular sludges a significant quantity of leach residue-jarosite solids are formed, e.g., 11.6 kg of solids or 17.8 kg of wet material (see Figure 6.1.) for a 17.1% Fe bearing sludge material. Therefore, the disposal of 17.8 kg would be required instead of 45.4 kg or approximately forty percent of the original sludge weight. A significant quantity of sludge material exists that has iron contents much lower than the above values. The jarosite process is also effective for treating the low iron containing sludges, e.g., two-four percent iron. The quantity of leach residue-jarosite solids produced from such sludge material would be rather small, e.g., a sludge similar in composition to the Figure 6.1 material but containing two percent iron would yield 5.6 kg of leach residue-jarosite solid. This quantity of solids translates, at 65% solids, to 8.6 kg of disposable material instead of 45.4 kg or approximately one-fifth the original sludge weight. Jarosites are widely produced in the zinc industry. They are deposited in lined storage ponds. It is difficult to state whether their heavy metal content means that the jarosite should be considered a hazardous material but even if that is the case at least a significantly smaller weight of material must be considered for disposal.

High iron sludges do (low iron sludges do not) present a problem for chromium recovery. Significant amounts of chromium are lost when the jarosite precipitation is performed. It is believed that the loss can be minimized by maintaining conditions such that chromium is not oxidized and the pH is maintained below 2.5. A releach of the jarosite solids appears to be necessary, if the sludge is a phosphorus containing sludge, to prevent both chromium and copper loss.

Mechanical control of the system is no problem. Chemical control must be exercised to ensure that the pH is maintained in the range 1.8-2.5 and that the iron is in the ferric form. Solid-liquid separation is effectively accomplished by allowing the leach residue-jarosite to settle; decanting the solution from the solids; and pumping the small volume of remaining slurry to a filter press.

- The removal of copper is accomplished by solvent extraction (SX). The extraction of copper from zinc, chromium, nickel and aluminum is selective and effective (>96% extraction per contact stage). Copper contents of a few mg/liter are achievable in two stages of contact and one stage of strip. The pH of the solution exiting the jarosite precipitation unit operation can be treated without adjustment.

The SX testrack is designed to treat up to 200 liters of solution per day. The design throughput is 500 cc/min. for each phase. Most tests to date have been performed at 250 cc/min. Ten contact mixer-settler units are available for copper SX. Therefore, this unit operation is not the slow step in treatment sequence, i.e., three concurrent streams could be treated (each in three cells) at one time; at 250 cc/min., 360 liters could be treated per day.

Large scale testwork has been conducted for up to six hours. Control of flowrate and interface levels is easily achieved and requires constant attention only during initial loading of the system. Once the system interfaces have been established little operator attention is required.

°The removal of zinc is accomplished by solvent extraction. The extraction of zinc from chromium and nickel is selective. Ferric iron, aluminum and calcium are partially coextracted with the zinc.

The extraction of iron (only between 0.2-0.6 gpl present) with zinc is desirable because it provides a way of removing residual iron from the solution. The iron once extracted into the organic is not stripped by H_2SO_4 but is stripped by HCl acid (4-6N). Zinc is stripped by H_2SO_4 (200 gpl). Therefore, a means of bleeding iron from the process stream is to load iron and zinc into the organic phase, strip the zinc by contacting with H_2SO_4 (200 gpl) followed by stripping the iron from the organic by contacting with HCl (4N). Both strip solutions can be recycled until the metal content is appropriate for recovery of zinc as zinc sulfate heptahydrate and for disposal of iron as ferric chloride solution.

Calcium is coextracted with zinc but poses no problem because it precipitates as gypsum in the H_2SO_4 strip circuit. It can be effectively filtered continuously from the solution during solution crystallization of zinc sulfate.

The zinc SX testrack is the same design as used for copper removal. Ten SX cells are available. The removal of 5 gpl zinc requires four stages of extraction, three stages of zinc stripping, and one stage of iron stripping. Therefore, the removal of zinc is the limiting step in the present treatment process. Two hundred liters can be treated at a flow rate of 400 cc/min. for each phase in an eight hour period. Some flexibility does, however, exist by control of the extracting reagent concentration in the organic and by changing the organic to aqueous ratio in the system.

Control of flowrate and interface levels is easily achieved and does not require constant attention once the initial loading and interface levels have been established; i.e., operator attention is minimal. The system can be shut off and restarted without difficulty. Chemical control of pH is required in zinc extraction to achieve effective zinc removal. Solution pH control is exercised by adjusting pH after the first two-stages of contact. Temperatures in the range of 40-55°C are desirable for rapid phase disengagement.

- Chromium removal is accomplished by first oxidizing chromium with chlorine gas, then precipitating lead chromate. The oxidation is more rapid if the chromium is present as chromium hydroxide and the system pH is maintained above four. Effective and rapid oxidation on a small laboratory scale has been accomplished. The reactor design used for large scale work was not as effective. Four to five hours of contact were required in the large scale testwork. Small and large scale testwork has also been performed using electrochemical oxidation in a partitioned electrode chamber cell. The results were encouraging and should be pursued further.

  Chromium removal is very effectively achieved by precipitation of the dichromate anions using lead sulfate. The removal of chromium is selective over nickel, i.e., nickel cations are not coprecipitated with the chromium. The process is one in which lead sulfate is regenerated for reuse, i.e., lead chromate can be redissolved in sulfuric acid to form chromic acid while reprecipitating lead sulfate. The precipitation of lead chromate from the oxidized leach solution is very rapid (one half hour). The lead chromate product is crystalline and dense. It settles rapidly and the solid-liquid separation is very easy and rapid.

  Mechanically the system operates easily. Chemical control is required to maintain the pH in the range 3.5-4.5.

- Nickel is removed by sulfide precipitation. The reaction is rapid and near quantitative removal is possible. The pH is maintained in the range 4-5 to ensure that hydrogen sulfide is not released. The solids are readily filterable.

  In actual practice a deficiency of sodium sulfide would be used, i.e., less than the stoichiometric requirement to completely precipitate the nickel. This procedure would leave some nickel in the solution but the presence of nickel is not a disadvantage because the final solution is recycled to the leach unit operation. Several alternate nickel recovery processes are possible.

6.2. LARGE SCALE SEQUENTIAL TEST MASS BALANCE (LOW IRON)

A flowsheet summarizing large scale experimental studies for low iron bearing solutions is presented in Figure 6.3. Included are mass balances for Cu, Fe, Zn, Cr, Ni, Cd, Al and Ca. The major difference in this flowsheet and

Figure 6.3 Treatment of 4.5 kg (100 lbs.) of low iron metal hydroxide sludge per day: element distribution

45.4 kg (100 pounds)/day

	Volume or Mass		Concentration (kg/day or %)						
			Fe	Cu	Zn	Cr	Ni	Al	Ca
1. Sludge (25.0 solids) :	11.4 kg solids	kg	0.66	0.68	0.91	1.52	2.04	0.32	0.09
	34.0 kg solution	%	5.8	6.0	8.0	13.3	17.9	2.8	0.8
2. Recycle Solids (35% solids):	0.5 kg solids	kg	0.01	0.00	0.0	0.21	0.00	0.06	0.00
	0.9 kg solution	%	1.6	0.0	0.0	35.0	0.0	10.0	0.00
3. Recycle Solution :	188.0 l	kg	0.0	0.0	0.0	< 0.01	< 0.01	0.00	0.00
4. H_2SO_4 Acid :	6.1 l (25.1 lbs.)								

↓

Acid Leach

- ·40-60°C
- ·0.5 hr.
- ·pH = 0.5-1.5

	Fe	Cu	Zn	Cr	Ni	Al	Ca
Extractions (%):	92.0	93.7	95.1	96.5	95.9	96.9	15.0

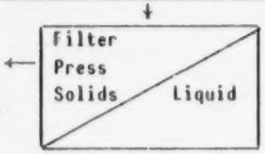
↓ pH = 1.0-1.5

	Volume or Mass		Concentration (kg/day or gpl)						
			Fe	Cu	Zn	Cr	Ni	Al	Ca
5. Leach Solution :	248 l	gpl	2.44	2.57	3.48	5.87	7.85	1.24	0.05
			0.61	0.63	0.86	1.46	1.95	0.31	0.01
6. Residue Solids :	3.2 kg (dry basis)	kg	0.05	0.04	0.04	0.06	0.08	0.01	0.08
		%	1.7	1.3	1.4	1.8	2.6	0.3	2.4

↓

Figure 6.3. (Continued)

Leach residue to disposal
(70% solids) 3.24 kg solid
1.39 kg solution
(composition as above: Stream 6



← 11 l wash water

pH = 1.5

7. Filtrate : 258 l

		Concentration (kg/day or gpl)					
	Fe	Cu	Zn	Cr	Ni	Al	Ca
gpl	2.33	2.46	3.33	5.61	7.50	1.19	0.05
kg	0.60	0.64	0.86	1.45	1.94	0.31	0.01

****

8. 0.6 NaOH (500 gpl)

Solvent Extraction of Copper
- Initial pH = 1.75
- Temp. = 40-50°C
- Three-stage extraction, O/A = 1
- Two-stage strip, O/A = 1, 180 gpl H_2SO_4
- 15 v/o LIX-622, 85 v/o KERMAC 470B
- 250 cc/min. each phase

← Extraction Efficiency: Stage 1 (pH = 1.75): 92.1%
Stage 2 (pH = 1.50): 85.2%
Stage 3 (pH = 1.30): 43.8%
Overall : 99.3%

****

→ 9. Copper may be electrowon (0.73 kg)
or
crystallized as $CuSO_4 \cdot 5H_2O$ (2.43 kg)

****

pH = 1.3

****

10. Raffinate : 260 l

		Concentration					
	Fe	Cu	Zn	Cr	Ni	Al	Ca
gpl	2.33	0.02	3.33	5.61	7.50	1.19	0.05
kg	0.60	0.01	0.86	1.45	1.94	0.31	0.01

****

Figure 6.3. (Continued)

11. 3.0 l NaOH (500 gpl)

Solvent Extraction of zinc and Iron
- Temp. = 40-50°C
- Four-stage Extraction O/A = 1
- Three-stage H_2SO_4 Strip
- 40 v/o DEHPA, 60 v/o KERMAC 510
- 250 cc/min Each Phase
- HCl (6 N)
- H_2SO_4 (200 gpl)
- pH 1.3 Into Cell One
- pH Adjusted to 2 Into Cell Two

	Extraction Efficiency				pH
	Fe	Zn	Ca	Al	
Cell 1	80.0	35.0	18.8	23.0	1.3
2	82.0	88.0	30.9	59.0	2.0
3	55.0	65.0	46.7	28.0	1.5
4	25.0	30.0	41.5	18.4	1.3
Overall	98.7	98.2	80.0	81.5	

****

12. Iron as $FeCl_3$ in HCl (see Section 8.4): 0.59 kg Fe
Zinc as $ZnSO_4$ in H_2SO_4:
Solution Composition:

	Zn	Al	Ca
kg	0.84	0.25	0.01

pH = 1.3

****

13. Raffinate : 263 l

	Concentration						
	Fe	Cu	Zn	Cr	Ni	Al	Ca
gpl	0.03	0.02	0.06	5.60	7.50	0.22	0.00
kg	0.01	0.00	0.02	1.45	1.94	0.06	0.00

****

14. 8 l 500 gpl NaOH

Chromium Oxidation
- Initial pH = 4-5
- Temp. = 30-50°C
- Retention Time = 4-5 hrs.

Oxidation Efficiency: 85%

****

15. Precipitate (35% solids): 0.5 kg solids, 0.9 kg solution

	Fe	Cr	Al
kg	0.01	0.15	0.02
%	2.0	30.0	4.0

pH = 4-5

****

Figure 6.3. (Continued)

16. Oxidized Solution : 270 l

	Fe	Cu	Zn	Cr	Ni	Al	Ca
gpl	0.00	0.00	0.06	4.79	7.28	0.15	0.00
kg	0.00	0.00	0.02	1.30	1.94	0.04	0.00

17. Lead Sulfide (2X Stoichiometric requirement) : 15.16 kg

* * *

pH = 3.5-4

Chromium Precipitation
·Temp.: Ambient
·Time: 0.5 hr.
·2X Stoichiometric Requirement of $PbSO_4$
·Initial pH = 3.5-4

← 18. 1 liter 500 gpl NaOH

* * *

→ 19. $PbCrO_4$-$PbSO_4$ (70% solids): 15.7 kg $PbSO_4$-$PbCrO_4$

	Cr	Al
kg	1.30	0.04
%	8.3	0.3

* * *

pH = 3.5-4

* * *

20. Solution : 280 liters

	Concentration						
	Fe	Cu	Zn	Cr	Ni	Al	Ca
gpl	<D.L.	<D.L.	0.06	0.008	7.28	--	--
kg	--	--	0.02	<0.00	1.92	--	--

21. Na_2S Solution (325 gpl) : 8 l

* * *

Figure 6.3. (Continued)

Nickel Precipitation
- Temp. = 25-35°C
- Time = 0.5 hr.
- 1X Stoichiometric Requirement of Na_2S (not optimized)
- Initial pH = 3-4

← 0.5 l 400 gpl H_2SO_4

→ 22. Sulfide Precipitate (35% solids): 3.0 kg solids
5.6 kg solution

	Ni	Cr	Zn	Al
kg	1.92	0.00	0.02	0.00
%	64.0	--	0.7	--

pH = 3-4

		Concentration						
		Fe	Cu	Zn	Cr	Ni	Cd	Al
23. Recycle Solution (to leach and to water makeup):292 liters	gpl	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.

↓

To Recycle

that presented in Figure 6.1 is that jarosite precipitation is not required. Iron is removed from the system solution by solvent extraction using D_2EHPA as the extractant with subsequent ferric ion recovery from the organic phase by stripping with hydrochloric acid solutions.

A summary of the distribution of each element is presented in Tables 6.4 and 6.5. The metal content of each solid product is presented in Table 6.6. The distributions are based on data generated in the large scale and continuous testwork presented in Section 8.4.

A major advantage of this flowsheet over the high iron flowsheet is the elimination of the jarosite precipitation unit operation. Therefore, copper and chromium loss does not occur and less disposable solids are created.

The throw away product is the leach residue; i.e., there are about 11,400 grams (25.0 pounds) of solids in the starting 45,400 grams (100 grams of sludge); from the leach of this solid material 3,200 grams of leach residue remains for disposal.

A list of summary comments for each large scale unit operation is presented below. A detailed presentation and discussion of all testwork are presented in Section 6.3 and Appendices 8.4 and 8.8.

- The sulfuric acid leach operation for the low iron bearing sludge is the same as presented previously, p. 71 .

- Solid/liquid separation of the leach residue can be successfully accomplished by use of a filter aid, e.g., Udylite Oxyfin 985. Pressure filteration is ineffective (the filter cloth plugs) in the absence of a filtering aid.

- The removal of copper is accomplished by solvent extraction as described previously, p. 72 .

- The removal of iron is accomplished by solvent extraction of iron with D_2EHPA in the first stage of the zinc extraction testrack. The pH of the aqueous phase is decreased to approximately 1.0, then contacted with a forty volume percent D_2EHPA - 60 volume percent KERMAC 510B kerosene. Iron is extracted leaving the zinc, nickel, and chromium in the aqueous solution. Some zinc is coextracted but

TABLE 6.4. TREATMENT OF METAL HYDROXIDE SLUDGE (LOW IRON) : ELEMENT DISTRIBUTION SUMMARY

			Distribution (kg/day)						
Input or Product (see Figure 6.3)	Mass (kg)	Volume (l)	Fe	Cu	Zn	Cr	Ni	Al	Ca
Stream No.									
1. Sludge	11.4 solids	34.0 kg-solution	0.66	0.68	0.91	1.52	2.04	0.32	0.09
2. Recycle Solids	0.5 solids	0.9 kg-solution	0.01	0.00	<D.L.	0.21	0.00	0.06	<D.L.
3. Recycle Solution		188.0 l	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.
4. H_2SO_4 Acid		6.1 l							
5. Leach Solution		248.0 l	0.61	0.63	0.86	1.46	1.95	0.31	0.01
6. Residue Solids	3.2 kg	1.4 kg-solution	0.05	0.04	0.05	0.06	0.08	0.01	0.08
7. Filtrate		258.0 l	0.60	0.63	0.86	1.45	1.94	0.31	0.01
8. NaOH (500 gpl)		0.6 l							
9. Copper Strip		7.5 l Aqueous	----	0.63	0.00	0.00	0.00	0.00	0.00
Circuit		7.5 l Organic							
10. Cu Raffinate		260.0 l	0.60	0.01	0.86	1.45	1.94	0.31	0.01
11. NaOH (500 gpl)		3.0 l							
12. Zinc and Iron		11.5 l H_2SO_4 (200gpl)	0.00	0.00	0.84	0.00	0.00	0.12	0.01
Strip Circuit (18.8 lit. org)		7.5 l HCl (6N)	0.59	-	-	-	-	0.13	-
13. Zinc and Iron Raffinate		224.0 l	0.01	0.00	0.02	1.45	1.94	0.06	0.00
14. NaOH (500 gpl)		8.0 l							
15. (same as #2)	0.5 solids	0.9 kg-solution	0.01	0.00	<D.L.	0.15	0.00	0.02	0.00
16. Oxidized Solution		278.0 l	0.00	0.00	0.02	1.30	1.94	0.04	0.00
17. Lead Sulfate	15.2 kg								
18. NaOH (500 gpl)		1.0 l							
19. $PbCrO_4$-$PbSO_4$	15.7 solid	6.7 kg-solution	0.00	0.00	0.00	1.30	0.00	0.04	0.00
20. Solution		292.0 l	0.00	0.00	0.02	0.00	1.94	0.00	0.00
21. Na_2S Solution (325 gpl)		8.0 l							
22. Sulfide Precipitate	3.0 solid	5.6 kg-solution	0.00	0.00	0.02	0.00	1.94	0.00	0.00
23. Recycle Final Soln.		259.0 l	<D.L.	<D.L.	<D.L.	<0.01	<0.01	<D.L.	<D.L.

TABLE 6.5. TREATMENT OF METAL HYDROXIDE SLUDGE (LOW IRON): DISTRIBUTION TO SPECIFIC PRODUCTS

Distribution to Specific Product	Distribution (%)						
	Fe	Cu	Zn	Cr	Ni	Al	Ca
Leach Residue	7.6	5.9	5.5	3.9	3.9	3.1	88.9
Copper SX Circuit	0.0	92.6	0.0	0.0	0.0	0.0	0.0
Zn and Iron SX Circuit	90.9	1.5	92.3	0.0	0.0	78.1	11.1
Chromium Slurry Oxidation Solid (Recycled to Leach)	1.5	0.0	0.0	9.9	0.0	6.3	0.0
Lead Chromate-Lead Sulfate	0.0	0.0	0.0	85.6	0.0	12.5	0.0
Sulfide Precipitate	0.0	0.0	2.2	0.0	95.1	0.0	0.0

NOTES:
- Distribution balance based on flowsheet Figure 6.3.
- Detailed experimental results for large scale sequential testwork presented in Section 8.13.

TABLE 6.6. TREATMENT OF METAL HYDROXIDE SLUDGE (LOW IRON): ELEMENTAL CONTENT IN SOLID PRODUCTS

Product	Elemental Content (%)						
	Fe	Cu	Zn	Cr	Ni	Al	Ca
Starting Sludge (Solids)	5.8	6.0	8.0	13.3	17.9	2.8	0.8
Leach Residue	1.6	1.2	1.6	1.9	2.5	0.3	2.5
Lead Chromate-Lead Sulfate 48.3% $PbSO_4$, 50.4% $PbCrO_4$, 1.3 $Al(OH)_3$	0.0	0.0	0.0	8.3	0.0	0.3	0.0
Nickel Sulfide	0.0	0.0	0.7	0.0	64.6	0.0	0.0

NOTES: ·Based on flowsheet Figure 6.3.

·Detailed experimental results for large scale sequential testwork presented in Section 8.13.

is stripped by 200 gpl sulfuric (iron does not strip). The iron bearing organic phase is then stripped with 6 N HCl and returned to the testrack for contact with the aqueous phase (at pH 2-2.5) for zinc loading.

The hydrochloric acid strip solution effectively removes the iron from the D_2EHPA but a problem with this approach is the relatively large quantity of strip acid required. The hydrochloric acid solution will only load iron to 5-9 gpl iron. Therefore, HCl recovery and recycle would be necessary in a commercial operation. Hydrochloric acid can be recovered from the strip solution by an additional solvent extraction unit operation. Recovery of hydrochloric acid was not investigated in this study but is practiced commercially by Tecnicas Reunidas Company at its Espindesa plant.

The removal of iron from the leach solution is effective; solutions containing <50 ppm iron can be produced. In the early stages of the study of this flowsheet crud formation in the first contact mixer and settler was a problem. In iron-phosphorus bearing solid phase developed. The use of a low pH in the first contact cell and a low aromatic kerosene eliminated this problem.

The removal of zinc is accomplished by solvent extraction. The zinc and iron solvent extraction system is one continuous system. A large fraction of the iron is loaded in the first stage of the testrack at a pH of about one. Zinc extracted into the organic phase of cell one is stripped by contact with 200 gpl H_2SO_4; then iron is stripped from the organic by 6 N HCl. The organic stream then then enters the second loading cell where it contacts the aqueous leach solution (at pH = 2-2.5). Zinc and iron are loaded into the organic in three stages of contact; then stripped in three subsequent stages of sulfuric stripping.

Comments presented previously, p. 73 , apply to zinc solvent extraction.

The unit operations for the removal of chromium and nickel described on page 73 to 74 are applicable also to this flowsheet reference.

6.3. UNIT OPERATION STUDIES

The discussion material presented in this section will be a summary of results. Tables and figures will be presented to support each unit operation summary. Support data and detailed discussion of experimental results and discussion of alternate treatment possibilities are presented in Appendices 8.2-8.14. Some studies presented in the appendix section are not discussed here. These were studies performed to guide the research team in their selection of the most appropriate flowsheet but whose results were not favorable enough to warrant further consideration.

The experimental approach and philosophy for the laboratory verification studies include preliminary test of concept by screening experiments; development of a two-level factorial design matrix for the experimental bench scale studies; execution of the studies in the design matrix to establish which variables are most important and what the relative effect of each particular variable is on the measured result; and subsequent use of the design matrix effects (by using the Box-Wilson "steepest ascent" approach) to optimize the selection of experimental variables for further larger scale testwork.

6.3.1. Leach Studies (Detailed discussion and data presented in Appendix 8.2)

6.3.1.1. Preliminary Testwork (Phase I)

Mixed metal sludge material was supplied by three sources in the Seattle, WA, area; i.e., two electroplating firms and a chemical disposal firm. Sludge compositions are, of course, variable and depend on many factors; such as electroplating activity at a particular plant at a particular time; mixing of spent liquor streams, etc. An illustration of composition variability between sources and even within a particular source was presented previously in Tables 4.1 and 4.3.

Three leach concepts have been considered, i.e., sulfuric acid leaching, chlorine gas oxidative leaching, and caustic leaching. Sulfuric acid leaching will be discussed in this section; oxidative leaching and caustic leaching are discussed in Appendix 8.13.

The sludge materials used in this study are designated by barrel number. All materials used in the experimental program were mixed metal sludges containing approximately twenty-thirty weight percent solids. The sample preparation procedure used to prepare sludge for testwork was: withdraw a 500 gram sample; mix and blend; sample at the time of a designated test to determine moisture content; chemically characterize the starting sample;

withdraw a specified weight of sample from the 500 gram batch for leach testing. Experimental reproducibility of the starting sludge solid composition for a specific blended sample is presented in Table 6.10.

Sulfuric acid is a very effective leaching agent for treating mixed metal sludge material. Based on design matrix and optimization studies a standard leach was chosen for all subsequent leach tests, i.e., the leach conditions used in a majority of the subsequent testwork were: 1/2 hour exposure; agitation to completely suspend all particles in the solution phase; temperature, 45-55^{0}C; solid/liquid ratio, 200 gm sludge/250 cc added solution; H_2SO_4 acid content, 100% of solid weight (70-100 gpl H_2SO_4, stoichiometric requirement for a typical test is ≈70 gpl).

A large number of leach tests, both in a kettle reactor system and on a larger scale confirm that sulfuric acid extractions are excellent. Typical leach results are presented in Table 6.8.

The residue from the leach test does not pass the EP toxicity test; Table 6.9. This is a preliminary conclusion that needs to be verified or disproven during a pilot scale study. The preliminary conclusion is based on EP test results on three design matrix test residues.

The weight of residue remaining after a typical leach test is approximately fifteen percent of the starting solids. The final leach residue is made up primarily of very finely divided iron and silica bearing compounds. Example compositions are presented in Section 8.2.

6.3.1.2. Large Scale Leach

The large scale leach testwork produced a concentrated leach solution, e.g., leach of Barrel one sludge produced 30 liters containing (in gpl): 11.16 Cu, 20.47 Fe, 18.04 Zn, 1.76 Cr, 7.96 Ni, 1.14 Cd, 4.61 Al; leach of Barrel 18 sludge produced 212 liters containing (in gpl): 3.25 Cu, 9.73 Fe, 5.27 Zn, 3.92 Cr, 1.21 Ni, 0.08 Cd, and 1.74 Al. Note the difference between Barrel one and 18 concentrations. The test assembly is limited by the iron and zinc

TABLE 6.7. STARTING SLUDGE MATERIAL BLENDED SAMPLE REPRODUCIBILITY

Test No.	Composition in Solid (%)										
	Cu	Fe	Zn	Cr	Ni	Al	Cd	Ca	Pb	Na	P
					Barrel 5 (used in kettle test)						
227	2.41	11.33	8.40	1.36	5.08	4.05	0.39	1.08	0.09	0.68	-
228	2.41	11.88	8.45	1.35	4.08	4.15	0.41	1.00	0.10	0.57	-
229	2.48	11.65	8.75	1.35	5.08	4.55	0.41	1.10	0.09	0.78	-
Average	2.43±0.05	11.62±0.29	8.53±0.22	1.35±0.01	4.99±0.91	4.25±0.20	0.40±0.01	1.06±0.04	0.09±0.01	0.68±0.10	
					Barrel 18 (used in large scale test)						
2486	8.26	19.05	6.15	8.52	1.91	2.66	----	0.31	0.08	0.57	4.01
2487	6.57	18.06	8.61	7.10	2.23	2.81	0.04	0.45	0.08	0.52	3.78
2488	6.03	17.37	9.99	6.24	2.28	3.13	0.08	0.44	0.07	0.65	3.19
2489	4.41	17.16	9.83	4.46	2.45	2.77	0.12	0.64	0.05	0.53	2.69
2490	4.05	16.91	6.96	4.13	2.47	2.58	0.11	0.64	0.11	0.41	2.54
Average	5.86±2.36	17.71±1.34	8.31±2.16	6.09±2.43	2.27±0.35	2.79±0.34	0.09±0.03	0.50±0.19	0.08± .03	0.54±0.11	3.24±0.70

TABLE 6.8. TYPICAL SULFURIC ACID LEACH OF MIXED METAL HYDROXIDE SLUDGE: STANDARD CONDITIONS

Test No.	Condition	Metal Extracted (%)						
		Fe	Cu	Zn	Ni	Cr	Cd	Al
535	100 gm sludge	92.0	93.7	95.9	95.9	96.5	93.0	89.9
942	650 gm sludge	95.4	94.9	90.5	97.8	96.7	100.0	95.7
532	1,000 gm sludge	55.8	94.3	94.2	85.0	96.7	97.0	96.0
2492	50,600 gm sludge	92.0	93.7	95.1	95.9	96.5	93.0	96.9

Notes:
- Standard conditions: one-half hour leach; ambient temperature; sludge/liquid ratio = 0.8; acid content equivalent to weight of solids in sludge.
- Detailed experimental results presented in Sections 8.2 and 8.13.

TABLE 6.9. E.P. TOXICITY PROCEDURE APPLIED TO LEACH RESIDUES: EXPERIMENTAL RESULTS

Sample	E.P. Leach Procedure Results (mg/l)										
	Cu	Fe	Cr	Ni	Zn	Cd	Si	Al	Ca	P	Pb
370	5.88 (5.91)	<0.006 (<0.006)	2.17 (2.17)	59.8 (56.8)	412.1 (388.3)	10.17 (8.91)	< 0.006 (< 0.006)	2.13 (3.27)	29.4 (28.4)	<0.076 (<0.076)	1.31 (1.30)
371	9.00 (8.99)	6.65 (3.92)	1.81 (2.02)	151.5 (146.0)	401.9 (412.1)	12.48 (11.65)	< 0.006 (< 0.006)	25.30 (23.84)	43.0 (42.8)	2.58 (2.95)	2.53 (3.24)
372	12.04 (12.39)	<0.006 (<0.006)	2.18 (2.28)	92.42 (93.31)	132.4 (137.1)	6.27 (5.19)	< 0.006 (< 0.006)	4.28 (3.01)	22.62 (23.22)	10.31 (3.79)	<D.L. (<D.L.)
373	24.51 (24.4)	<0.006 (<0.006)	0.39 (0.42)	129.5 (134.7)	648.1 (650.8)	94.06 (97.0)	< 0.006 (< 0.006)	0.60 (1.41)	585.1 (584.1)	14.4 (19.6)	1.76 (<D.L.)

See Table 8.2 for leach conditions to produce residue for E.P. Test; residue 370 resulted from matrix test 261; residue 371 resulted from matrix test 291; residue 372 resulted from matrix test 356.

content in its ability to treat solutions, i.e., the jarosite precipitation unit operation cannot be used to effectively treat iron contents above about 10-15 gpl; the zinc solvent extraction unit operation cannot be used to effectively treat zinc contents above 5-6 gpl. Therefore, in some cases the solid/liquid ratio used in the leach was varied to produce the desired solution composition (of iron and zinc) or alternately concentrated leach solutions were diluted to achieve desired solution composition.

A number of large scale leach tests have been performed. The results are reported in the sequential data tabulation presented in Appendix 8.13, Tables 8.121-8.126. A summary of the large scale testwork is presented in Table 6.10. The extraction results are excellent and comparable to the results obtained in small scale testwork.

The large scale leach operation (75-100 pounds of sludge per day) can be accomplished in a single vessel in one-half hour reaction time; then the conditions changed to favor iron removal by jarosite precipitation and the iron removal operation performed in the same vessel. An alternate approach is to leach continuously in a much smaller reactor and store the solution for later jarosite treatment.

The leach residue has poor settling and filtration properties. The residue blinds the filtering media, i.e., filter papers (small tests) or filter cloths (large tests). The poor filterability of the leach residue was a major reason for adopting a treatment procedure based on precipitation of jarosite into the leach residue. This greatly enhances the solid-liquid separation process. A comparison of filterability between leach residue and leach residue-jarosite mixtures in the pilot scale filter press is presented in Appendix 8.5, Tables 8.63 and 8.64. Rates are tremendously different, e.g., leach residue, 4.5 kg/m^2/hr., leach residue-jarosite, 25-55 kg/m^2/hr. Most of the large scale solid/liquid separation testwork was, therefore, conducted on leach residue-jarosite mixtures. (This aspect of the study is discussed in more detail in Section 6.3.3 and Appendix 8.5.)

TABLE 6.10. SUMMARY OF LARGE SCALE LEACH TESTWORK

Test Designation	% Extracted						
	Fe	Cu	Zn	Ni	Cr	Cd	Al
Sequential Test: Series Four 15.9 kg (35 lbs.) sludge	62.3	75.9	83.8	82.4	84.6	90.0	90.3
Sequential Test: Series Five 50.4 kg (111 lbs.) sludge	92.0	93.7	95.1	95.9	96.5	93.0	96.9
Sequential Test: Series Six 22.7 kg (50 lbs.) sludge	65.0	92.0	96.9	92.1	92.3	100.0	90.6

NOTES: Standard H_2SO_4 leach conditions used for each test except sequential test series five. See Tables 8.126-8.127 for detailed results.

6.3.1.3. Large Scale Leach (Phase II)

The large scale leach on Phase II material was conducted in the same manner as in Phase I. The resulting leach solutions were high chromium, nickel bearing solutions, Table 6.11. these solutions were then doped (after solids removal) to achieve desired iron, copper and zinc contents for subsequent testwork.

The leach solids were removed from the solution using the filter press. Poor filterability of the leach residue was overcome by use of Udylite Oxyfin 985 filter aid. Filter rates comparable to jarosite filtration was achieved by use of 9.2 grams of filter aid per square decimeter of filter area. Detailed experimental data and discussion of results are presented in Appendix Section 8.5.

6.3.2. Iron Removal

6.3.2.1. Iron Removal from High Iron Bearing Solutions

Iron must be removed early in the treatment sequence because of its coextraction and therefore contamination of subsequent metal separations. However, alternates do exist as to where in the treatment sequence it is removed, e.g., iron can be removed prior to any other metal ion by jarosite precipitation from an acid solution or iron can be removed after copper extraction because the commercial reagents available for copper extraction are highly selective for copper over iron. The advantage of removing iron by jarosite precipitation prior to copper extraction is that the jarosite precipitation conditions appear to significantly improve the copper solvent extraction process phase separations. Shake tests for copper extraction (using commercial reagents) applied to untreated leach solutions produce system muck that hinders the separation of the organic and aqueous phases. However, shake tests (and large scale tests also) show much improved phase separation, after iron removal, i.e., the high temperature jarosite precipitation process produces a leach solution much simpler to treat for copper extraction.

TABLE 6.11. EXAMPLE LEACH SOLUTION COMPOSITIONS FOR PHASE II MATERIALS

Sample No.	Concentration (gpl)							
	Cu	Fe	Zn	Cr	Ni	Al	Ca	P
3208	-	1.728	2.425	6.471	2.502	0.029	0.702	-
3255	-	1.611	2.231	5.470	2.547	0.035	0.696	-
3459	2.750	3.899	-	1.987	5.847	0.207	0.317	0.572
3482	3.130	4.068	0.131	2.084	6.260	0.248	0.331	0.656
3542	2.600	4.237	0.300	2.238	6.815	0.353	0.369	0.627
3606	1.035	3.616	0.126	1.907	5.727	0.362	0.322	-
3619	2.045	3.117	0.099	1.725	5.019	0.354	0.303	-
3670	2.225	3.078	0.105	1.693	5.046	0.373	0.276	-

Notes: Standard Conditions: One-half hour leach; 40-55^{o}C; sludge/liquid = 0.8; acid content equal to weight of solid in sludge.

Iron can be removed by other alternate treatment processes. Such alternatives are discussed in Sections 8.3.2 and 8.3.4. The emphasis of this study was placed on removing iron, prior to any other metal, by selective precipitation as a jarosite compound. The detailed experimental results are presented in Section 8.3.1. Jarosite precipitation is a rather widely used commercial means of rejecting iron from an acid leach solution(6,7).

There are presently 16 commercial zinc plants using a jarosite precipitation process(1,6). All of these plants use either sodium or ammonium as the alkali ions. Potassium is used in several industrial treatment flowsheets; usually for those flowsheets that deal with the recovery of a high value product such as copper(8,9) and cobalt(10).

The extent of iron removal from a solution is system dependent. However, some generalities can be stated that assist in the design of an appropriate iron removal system, i.e., Dutrizac(1) has recently reviewed and summarized a great deal of literature on jarosite precipitation studies. The results of a portion of his review on the conditions affecting the precipitation of jarosite family compounds is paraphrased below:

- Sodium, Potassium and Ammonium Jarosites

  Jarosites for each alkali cation exist and can be readily formed. Most research has been performed on sodium and ammonium jarosites because of the lower reagent cost. A substantial body of research information exists for the jarosite families.

- Temperature

  Jarosites can be formed at room temperature but the rate of formation is very slow, e.g., potassium jarosite was formed at 25°C in a pH range of 0.82-1.72 but required four weeks to six months. Jarosite precipitation is quite rapid above 80°C. Commercially useful rates require temperatures greater than 90°C and sodium and ammonium require higher temperatures than potassium.

- pH

  Solution pH is very important in the jarosite precipitation process, i.e., the precipitation reactions produce acid and if the pH is not controlled the reaction is stopped. For example the jarosite precipitation reaction produces one mole of acid for each mole of

Fe^{+3} precipitated. Dutrizac presented the results of Babcan(11) for the pH-temperature stability of potassium jarosite, Figure 6.4. The pH range at which jarosite forms decreases in maximum value as the temperature is raised, i.e., at 20°C the range is 2-3, at 100°C it is 1-2.3. The present work was conducted in the range of 88-92°C at pH values of 2-2.7. A summary of the research results of several workers seems to suggest that the ideal range is 1.5-1.6 at 100°C.

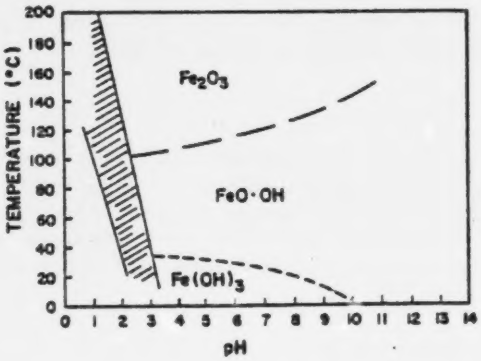


Figure 6.4. Stability field for potassium jarosite formation (hatched area) as a function of pH and temperature for jarosite formation from 0.5 M $Fe_2(SO_4)_3$ solutions at 20-200°C.

The critical pH at 90°C at which the crystallizing jarosite(12) (excellent filtering) transforms to an amorphous form (poor filtering) is

$$pH = 0.21 \log [Fe^{+3}] + 1.84 \quad \text{(0 grams per liter zinc)}$$

$$pH = 0.21 \log [Fe^{+3}] + 1.80 \quad \text{(100 grams per liter zinc)}$$

where $[Fe^{+3}]$ = grams per liter

·Alkali Concentration

The removal of Fe^{+3} appears to be essentially independent of alkali concentration. Slight excess stoichiometric amounts seem appropriate.

·Iron Concentration

Jarosites are readily precipitated from solutions containing 0.025-3.0 M Fe^{+3} (1.3-167.4 gpl). The lower limit for Fe^{+3} concentration appears to be about 0.001 M (50 ppm).

•Order of Stability

The extent of iron precipitation is in the order K > NH_4 ∼Na. Therefore, lower solution iron contents may be expected using K ions. The free energy of formation values(2) for the jarosites are: -788.6 Kcal/mole, -778.4 Kcal/mole, -736.2 Kcal/mole for K^+, Na^+, NH_4^+ respectively.

•Ionic Strength

Studies on formation of potassium jarosites from high ionic strength solutions show no appreciable effect.

•Seeding

The precipitation process is dependent on the presence of a seed. Most investigators suggest approximately 100 gpl seed. Recycling of seed is recommended so that large crystalline jarosite particles form in order to enhance the settling or filtration rate. In the present project the leach residue serves the function of a seed nucleation site.

•Final Iron Content Achievable

Industrially the jarosite process is used to decrease the iron content from very high levels to 1-2 gpl. The equilibrium relationship for ammonium jarosite at 100°C shows that very low iron content should be achievable(12):

$$\frac{[Fe^{+3}]}{[H_2SO_4]} = 0.004 \text{ (gpl)}$$

Plant practice shows equilibrium is not truly attained(12) and the relationship is:

$$\frac{[Fe^{+3}]}{[H_2SO_4]} = 0.01 \text{ (gpl)}$$

Therefore, low iron concentration is possible, e.g., at pH = 1 the $[H_2SO_4]$ = 4.9 gpl and $[Fe^{+3}]$ = 0.049 gpl or < 50 ppm.

The iron level achieved in the final solution depends on time, pH, temperature, and alkali ion used. The iron contents achieved in this study for large scale testwork usually was in the range of a few hundred mg/liter for the conditions: pH = 1.8-2.5, temperature = 88-92°C, K^+ alkaline ion, time 5-6 hours. Iron contents in the range of 200-500 mg/liter are considered appropriately low for subsequent zinc solvent extraction.

•Impurity Behavior

The partitioning of impurities to the jarosite product has been considered. The following generalities are noted. The extent of incorporation of impurities in the jarosite solid product increases:

- with increasing M SO_4 concentration in solution
- with increasing pH
- with increasing alkali concentration in solution
- with decreasing Fe^{+3} concentration in solution
- K jarosite > Na jarosite ∼ NH_4 jarosite.

The order of cation metal incorporation appears to be $Fe^{+3} >> Cu^{+2} > Zn^{+2} > Co^{+2} > Ni^{+2} > Cd^{+2}$.

A table describing the partitioning of impurities(13) between potassium jarosite and the solution is presented in Table 6.12. The K value is defined by the ratio:

$$\frac{\text{weight percent in jarosite}}{\text{concentration of impurity in solution (g/100 cc)}}$$

Saarinen(14) investigated the incorporation of Cr^{+3}, Co^{+2} and Ni^{+2} from solutions (the concentration levels not given) into sodium jarosite. His results showed incorporation to be low: 0.3-1.4 wt. % Ni^{+2}; 0.5-1.4 wt. % Co^{+2}; and 0.6-1.6 wt. % Cr^{+3} at 90°C in the pH range 1-2.

Some anions also are incorporated into the jarosite structure. Chromate may substitute completely for sulfate in jarosite compounds(3,4,15). Some anions co-precipitate with rather than incorporate in the jarosite structure. Dutrizac(1) has summarized the results of a number of studies dealing with anion behavior during jarosite precipitation. A portion of his results are presented in Table 6.13.

TABLE 6.12. RELATIVE PARTITIONING OF SOME IMPURITIES BETWEEN POTASSIUM JAROSITE AND THE SOLUTION PHASE (13)

Impurity	Initial Concentration (g/100cc)	K
Zn^{+2}	3.2 - 16.3	0.20 - 0.08
Cd^{+2}	0.056 - 1.2	0.02
Cu^{+2}	0.32 - 1.60	1.0 - 0.56
Mg^{+2}	0.78 - 1.65	0.013 - 0.006
Ni^{+2}	0.0015	0.7
Al^{+3}	0.63 - 1.4	1.4 - 1.3

TABLE 6.13. BEHAVIOR OF SOME ANIONS DURING JAROSITE PRECIPITATION (1)

Ionic Specie		Precipitation Behavior
CrO_4^{-2}		Substitutes for Sulfate in jarosite structure, $KFe_3(CrO_4^{-2})_2(OH)_6$
MnO_4^-	(>0.05 M)	Precipitates with ferric ion as poorly crystalline $(Mn, Fe)O_2$
	(<0.03 M)	Precipitates with jarosite as poorly crystalline $(Mn, Fe)O_2$
Si^{+4}	(>0.05 M)	Forms silica gel at 97°C
	(>0.03 M)	Does not precipitate
SnO_3^{-2}	(0.25-0.1 M)	Hydrolyzes to amorphous $(Sn, Fe)O_2$
MoO_4^{-2}		Precipitates with ferric ion as $Fe_2(MoO_4)_3$

Gordon and Steintveit(6) have reviewed possible jarosite disposal techniques. A good deal of effort has been expended to determine appropriate disposal techniques because jarosites in most cases have sufficient heavy metal ion content to require use of impermeable membrane lined storage areas. Treatment processes investigated include:

- Sulfation roasting to solubilize heavy metal salts and to produce pure iron oxide(16).
- Thermal decomposition and production of iron oxide(17-21).
- Hydrothermal decomposition to form iron oxide and recover soluble salts(22,23).
- Electric furnace smelting(24).
- Fertilizer(25), especially NH_4 and K jarosites.
- Fillers in asphalt or as an iron source in cement(26).

The results of the present study confirm the impoundment or burial of the jarosite product after thermal or air drying would be necessary. The EP test shows that the leach residue-jarosite product does release some heavy metals; Table 6.14. The quantity of leach residue-jarosite solid material produced by a waste treatment plant would, of course, be very dependent on the incoming iron content. The sludges studies in the first phase of this work were high in iron, 10-15 Wt. % of the solids. Much of the nation's mixed metal sludges are, however, not high in iron; usually less than 2 wt. % of the solids. The sludges studied in the second phase of the present work were low in iron, <4 wt. %.

Even if the leach residue-jarosite solids were considered hazardous, the quantity of material to be disposed of would be considerably less than the starting sludge material; e.g., the low iron sludges (<2 wt. % Fe) would produce approximately 0.02 gm jarosite solid/gm sludge (40 pounds/ton sludge); the high iron sludges (15 wt. % Fe) would produce approximately 0.15 gm jarosite solid/gm sludge (300 pounds/ton sludge).

TABLE 6.14. E.P. TOXICITY PROCEDURE APPLIED TO LEACH RESIDUE-JAROSITE SOLIDS PRODUCED FROM FULL SCALE (50.4 kg) TEST.

Sample	E.P. Leach Procedure Results (mg/l)									
	Cu	Fe	Zn	Cr	Ni	Cd	Al	Pb	Ca	P
2612	21.5	0.17	7.94	0.33	2.35	0.03	0.01	0.2[illegible]	19.2	13.0
2613	21.5	0.12	8.90	0.31	2.58	0.03	0.01	0.23	18.4	13.7
2614	21.5	0.11	8.55	0.30	2.60	0.03	0.01	0.35	18.9	13.8
2615	21.4	0.25	9.79	0.28	2.41	0.09	0.01	0.24	21.4	12.1
2616	21.3	0.16	9.51	0.24	2.31	0.04	0.01	0.15	20.9	10.9
2617	21.3	0.24	9.16	0.26	2.23	0.04	0.01	0.19	20.9	10.7

Notes:
. Tests performed according to EPA designated EP Toxicity test(27).
. Starting Leach residue-jarosite composition (%):

Fe	Cu	Zn	Cr	Ni	Cd	Al	Pb	Ca	P
19.8	2.8	0.28	3.20	1.20	0.10	1.70	0.10	0.23	3.19

. Large scale test performed on Barrel 18 sludge.
. EPA designated concentration of contaminants for characteristic toxicity (mg/l):

Cd	Cr	Pb
1.0	5.0	5.0

6.3.2.2. Iron Removal from Low Iron Bearing Solutions

Iron removal from low iron bearing solutions is difficult by jarosite precipitation. An alternative method of removal, by solvent extraction, was investigated. This unit operation depicted in the low iron flowsheet, Figure 6.3, follows copper solvent extraction whereas jarosite precipitation used on the high iron solution is conducted prior to copper solvent extraction.

The removal of iron from solutions containing a few grams per liter iron by solvent extraction using D_2EHPA-kerosene mixtures was experimentally investigated during the Phase II study. The envisioned advantages included: no loss of chromium during jarosite precipitation because of the removal of this unit operation and the generation of a smaller quantity of disposable solid residue.

D_2EHPA reagent has a selectivity for metal cations that is a strong function of pH, Figures 8.10a and 8.10b. At low pH levels iron is selectively extracted from an aqueous phase into the organic phase. A portion of the zinc is coextracted with the iron at a pH of about one but this can be effectively recovered selectively from the organic phase by sulfuric acid (200 gpl) stripping. Ferric ions are strongly bound within the organic phase and are not stripped easily. Sulfuric acid (at 200 gpl) will not strip the iron. Hydrochloric acid (4-6 N) will strip the ferric ions.

Experimental studies show excellent iron removal from leach solutions, e.g., iron contents were consistently lowered to <50 ppm. Other metal cations, except for zinc, are not co-extracted (Ni^{+2}, Cr^{+3}). The process looks favorable except for the fact that large quantities of hydrochloric acid is consumed. Therefore, recovery of hydrochloric acid would be required. There is one commercial operation that uses D_2EHPA loading and hydrochloric acid stripping with recovery of HCl by solvent extraction with Amberlite LA-2 (R_2NH_2Cl)(31).

Detailed experimental data and discussion of results for the solvent extraction of iron are presented in Appendix Section 8.5.

6.3.3. Solid/Liquid Separation

The separation of leach residue-jarosite solids from the solution phase is very effectively accomplished by settling and filtration. The major advantage of the jarosite process is the rapid filtration rate achievable. Industrial rates in the range 4,540-13,620 kgm residue/m^2·day (5-15 tons residue m^2·day) are achieved(2).

A description of the large scale filter press is presented in Section 8.4. The procedure used for solids separation was to leach the sludge, precipitate the jarosite into the leach residue, pump the slurry to a storage settler, allow the jarosite residue to settle, pump most of the solution off the settled solids, then to filter the remaining slurry through the filter press. The filter press has several unique features that allow the user to exercise a variety of operating-cake treatment options, e.g., top or side cake washing, cake compression, cake drying. Tests were not conducted to determine the best set of conditions for cake clean-up and recovery during the Phase I study because of the limited number of large scale tests performed. Even without optimizing the operating parameters cakes containing only thirty percent moisture were produced.

The operation of the filter press is straight forward and major problems were not encountered in the present study. It should be noted, however, that a coarse screen must be mounted to cover the slurry pump inlet hose to prevent small pieces of wood, glass, pebbles, etc., from entering the diaphragm pump.

6.3.4. Copper Solvent Extraction

Commercial copper solvent extraction processes are described in detail in a recent publication(28), The Handbook of Solvent Extraction (1983). A significant portion of the World's copper is produced by solvent extraction, e.g., world copper production capacity by SX is over 500,000 tons/year. The technology is, therefore, well developed.

Several reagents are used commercially but all belong to the hydroxyoximes family: A comparative summary of the three major reagents is presented in Table 6.15.

TABLE 6.15. COPPER SOLVENT EXTRACTION COMMERCIAL REAGENTS(29)

Trade Name	Composition	Comments
LIX 64N (Henkel Corp.)	2-Hydroxy-5-nonyl benzophenone oxime (LIX-65N) plus 5,8-Diethyl-7-hydroxy-6-dodecanone oxime	Standard Reagent for low copper bearing sulfate aqueous solutions; usually applied to solutions with <2 gpl Cu
P 5100 (Acorga, Ltd.)	Substituted salicyl aldoxime plus equal amount of nonyl phenol	Strong chelating agent. Useful for high copper bearing sulfate solutions
LIX-622 (Henkel Corp.)	Not reported in literature	Strong chelating agent. Useful for high copper bearing sulfate solutions. Requires high (180-200 gpl) acid for stripping

Commercial copper solvent extraction has been applied primarily to dump and heap leach operations. Very little study has been devoted to its use on complex metal bearing solutions. The dump and heap leach processes are primarily iron and copper bearing sulfuric acid solutions whereas the sludge leach solutions contain copper, iron, nickel, zinc, chromium and sometimes aluminum, calcium and cadmium. It was, therefore, of interest and necessary to investigate whether SX would be selective toward copper over the other metal ion constitutents. The equilibrium distribution diagram(30) shows (Figure 6.5) that a pH can be selected at which copper should be extracted in preference to the other metals present.

The experimental procedure used in solvent extraction testwork is presented in Section 5.2.1. Small-scale shake tests were performed to determine appropriate experimental conditions for subsequent small-scale

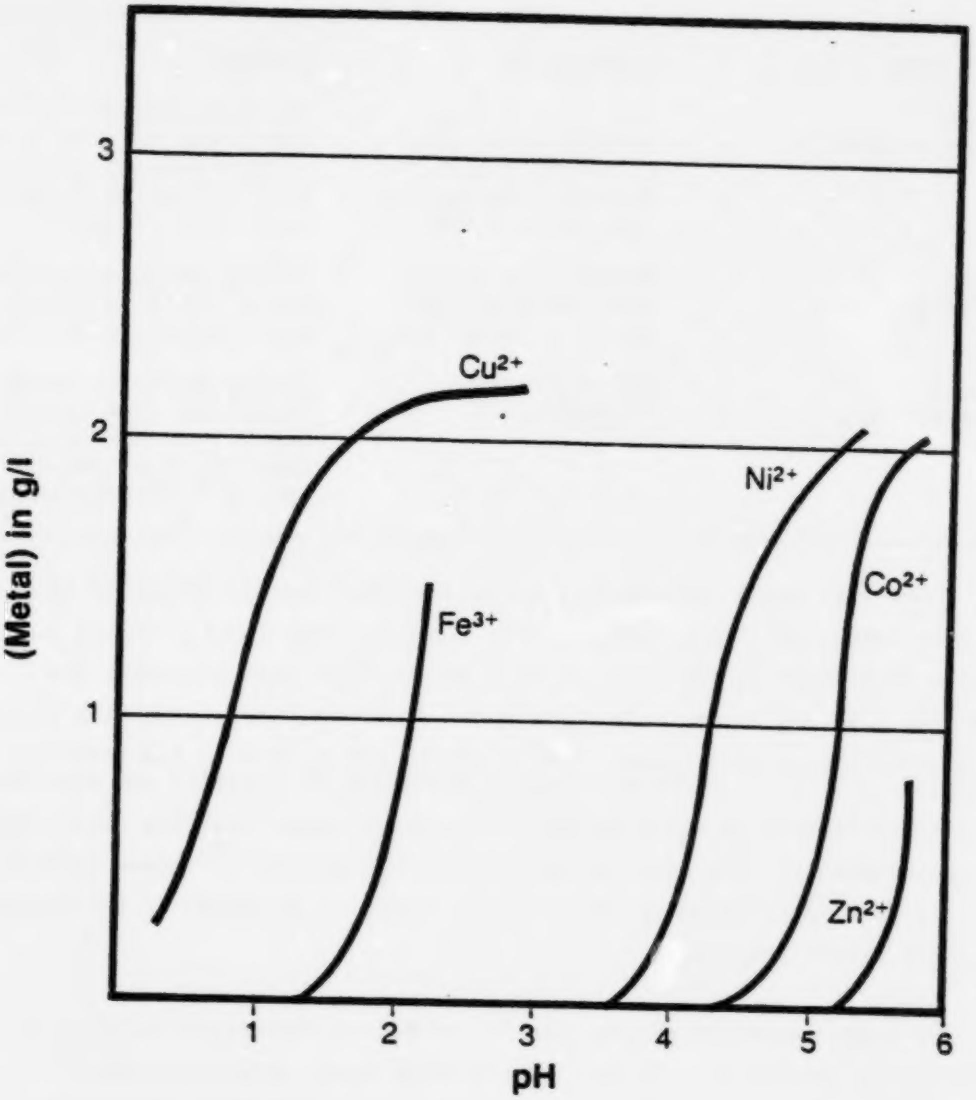


Figure 6.5. Equilibrium distribution diagram for LIX 64N. (From Kordosky(29))

continuous testwork and ultimately full-scale continuous testwork. The detailed experimental results are presented in Section 8.6, 8.8, and 8.13.

Small-scale testwork showed good selectivity and excellent phase separation in accordance with quoted literature conditions. Testwork was performed using LIX-64N , LIX-622, and ACORGA 5100. All appear appropriate for application to sludge leach solutions. Small-scale continuous testwork was performed using LIX-64N and LIX-622. LIX-622 was chosen for large-scale continuous testwork because of its high copper loading capabilities, its insensitivity (for good phase separation) to system temperature, and its fast loading and stripping capabilities.

Small scale continuous testwork on high iron containing solutions (>15 gpl Fe) showed a muck (see list of definitions, p. xxvi of this report) formation problem especially when aged (several weeks) solutions were used. Therefore, most of the subsequent research was performed on jarosited solutions. The jarosited solutions even when aged did not show a muck formation problem.

Large-scale testwork was performed in a Reister testrack (described and shown schematically in Section 5.2.1.2. and pictorally in Section 8.14). The experimental results for Phase I testwork for five large scale sequential tests are presented in Section 8.13. The test results for a five-day large scale test conducted during Phase II are presented in Section 8.6.2. An eleven day continuous copper extraction and organic degradation test study was conducted and the results are presented in Section 8.6.3. The copper extraction results for all the testwork are summarized in Tables 6.16 and 6.17. Degradation test studies were conducted in the large scale test system and in the bell Engineering testrack. The important considerations with request to organic reagent degradation are: the amount of aqueous phase that contacts the organic, effect of mixer action on stability or organic reagent to oxidation; and the effectiveness of the organic to function well over a large number of load/strip cycles.

TABLE 6.16. SUMMARY OF LARGE SCALE TESTS ON SOLVENT EXTRACTION OF COPPER WITH LIX 622

Sample No.	Condition	Copper Extraction From Leach Solution		
		Percent	Copper Content in Solution	
			Initial (gpl)	Final (gpl)
	Sequential Series One (Table 8.86)			
1524	Raffinate From Contact.(40 lit.)	98.9	1.37	0.017
	Sequential Series Two (Table 8.88)			
1816	Raffinate From Contact. (60 lit.)	94.4	0.39	0.022
	Sequential Series Three (Table 8.89)			
2005	Raffinate From Contact.(20 lit.)	98.0	2.32	0.047
	Sequential Series Four (Table 8.90)			
2146	Raffinate From Contact. (90 lit.)	96.9	3.89	0.120
	Sequential Series Five (Table 8.91)			
2146	Raffinate From Contact. (160 lit.)	99.0	3.05	0.030

Note: . Detailed results presented in Section 8.13.

TABLE 6.17. SUMMARY OF CONTINUOUS COPPER EXTRACTION: ELEVEN DAY LONG TERM ORGANIC EXPOSURE TEST RESULTS.

Sample No.	Condition	Copper Extraction From Leach Solution		
		Copper Concentration (gpl)		Copper Extracted (%)
		Initial	Final	
3458	Starting Solution	2.750		
3474	First Day Raffinate		0.054	98.0
3482	Starting Solution	3.130		
3493	Second Day Raff.		0.062	98.0
3501-B	Starting Solution	2.697		
3509	Third Day Raff.		0.106	96.1
3519	Starting Solution	3.332		
3533	Fourth Day Raff.		0.088	97.4
3542	Starting Solution	2.600		
3548	Fifth Day Raff.		0.039	98.5
3552	Starting Solution	0.835		
3567	Sixth Day Raff.		0.056	93.3
3606	Starting Solution	1.035		
3613	Seventh Day Raff.		0.033	96.9
3619	Starting Solution	2.045		
3631	Eight Day Raff.		0.027	98.7

(Continued)

TABLE 6.17. CONTINUED

Sample No.	Condition	Copper Extraction From Leach Solution		
		Copper Concentration (gpl)		Copper Extracted (%)
		Initial	Final	
3639	Starting Solution	1.812		
3643	Ninth Day Raff.		0.073	97.0
3657	Starting Solution	2.026		
3664	Tenth Day Raff.		0.043	96.0
3670	Starting Solution	2.225		
3703	Eleventh Day Raff.		0.049	97.8

Note: . Test conditions detailed in Table 8.81.

There was no apparent effect of continuous exposure of the recycled organic phase in the large scale system over 18 hours of cumulative exposure, Table 6.18; 14 1/2 liters of organic were exposed (two stages of load, two stages of strip) to 274 liters of aqueous leach solution. Therefore, the aqueous/organic contact ratio was 18.5.

A second series of continuous exposure tests was performed in the Bell Engineering testrack. There was no apparent effect of continuous exposure over 112.8 hours of cumulative exposure, Tables 6.19, 6.20. Three and eight-tenths liters of organic were exposed (three stages of load, two stages of strip) to 341.5 liters of aqueous leach solution. Therefore, the aqueous/organic contact ratio was 88 (approximately 226 load/strip cycles).

Detailed experimental results and further discussion are presented in Appendix Section 8.8.1.

6.3.5. Zinc Solvent Extraction

Commercial application of solvent extraction for zinc recovery is limited. However, for the treatment of solutions containing a mixture of zinc, chromium, and nickel the alternatives are few. The only large scale commercial application of zinc solvent extraction at present is in Spain; Technical Reunidos uses such a process at its Bilbao plant for the production of 8,000 tons/yr. of zinc. (Thorsen(31) discusses the commercial operation at Bilbao.)

The commercial reagent available for extraction of zinc (and cadmium) from acid solutions is the organo phosphoric acid; diethylhexylphosphoric acid (D_2EHPA). The equilibrium distribution diagram(30) illustrating zinc and other metal extraction as a function of pH is presented in Section 8.7. Zinc can be selectively extracted from an acid solution of pH $\sim$ 2 in the presence of chromium and nickel. Aluminum and calcium are not presented on the referenced distribution diagram. However, if these ions are present in the leach solution they will be partially co-extracted. Conditions can, in fact, be chosen so that zinc, aluminum and calcium are completely coextracted.

TABLE 6.18. LIX 622 ORGANIC EXPOSED IN LARGE SCALE TESTRACK FOR FIVE DAY TEST PERIOD.

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Copper Concentration in Aqueous Phase (gpl)	
			System Organic	New Organic
3271	Starting Aqueous Solution, 3.12 gpl Cu			
	First Day			
3286	65 liters	First	0.06	
3287	" "	Second	0.01	
3288	None	First		0.12
3289	"	Second		< 0.01
	Second Day			
3307	141 liters	First	0.08	
3308	" "	Second	0.01	
3309	None	First		0.07
3310	"	Second		< 0.00
	Third Day			
3339	209 liters	First	0.10	
3340	" "	Second	0.02	
3341	None	First		0.09
3342	"	Second		< 0.01
	Fourth Day			
3361	274 liters	First	0.13	
3362	" "	Second	0.01	
3371	None	First		0.08
3372	None	Second		< 0.00

TABLE 6.18. CONTINUED

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Copper Concentation in Aqueous Phase (gpl)	
			System Organic	New Organic
	Fifth Day			
3363	347 liters	First	0.08	
3364	" "	Second	0.01	

Notes:
. 15v/o LIX 622 in Kermac 470B Kerosene.
. 100cc of used organic stripped twice with 100cc clean 200 gpl H_2SO_4.
. Stripped system organic contacted with 100cc of No. 3271 aqueous at initial pH =1.54, 7 minutes, 25°C.
. New organic treated same as system organic but not exposed to leach solution before test.
. New organic treated with 30 gpl Cu, 200 gpl H_2SO_4 before use.

TABLE 6.19. LIX 622 LONG TERM EXPOSURE DEGRADATION TEST SUMMARY

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Copper Concentration in Aqueous Phase (gpl)	
			System Organic	New Organic
	Starting Aqueous Solution, 3.112 gpl Cu			
	First Day			
3478	46.5 liters	First	0.061	
3479	" "	Second	0.008	
3480	None	First		0.121
3481	"	Second		0.006
	Second Day			
3495	86.5 liters	First	0.103	
3496	" "	Second	0.027	
3497	None	First		0.031
3498	"	Second		0.000
	Third Day			
3514	125.5 liters	First	0.114	
3515	"	Second	0.016	
3516	None	First		0.035
3517	"	Second		0.016
	Fourth Day			
3536	161.5 liters	First	0.109	
3537	" "	Second	0.019	
3540	None	First		0.028
3541	"	Second		0.001

TABLE 6.19. CONTINUED

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Copper Concentration in Aqueous Phase (gpl)	
			System Organic	New Organic
	First Day			
3550	187.0 liters	First	0.001	
3551	None	First		0.040
	Sixth Day			
3615	206.5 liters	First	0.036	
3616	" "	Second	0.008	
3617	None	First		0.006
3618	"	Second		0.007
	Seventh Day			
3635	241.0 liters	First	0.112	
3636	" "	Second	0.022	
3637	None	First		0.024
3638	"	Second		0.007
	Eighth Day			
3647	275.5 liters	First	0.258	
3648	" "	Second	0.023	
3649	None	First		0.053
3650	"	Second		0.004
	Ninth Day			
3665	287.5 liters	First	0.120	
3666	" "	Second	0.000	
3667	None	First		0.015
3668	"	Second		0.020

TABLE 6.19. CONTINUED

Notes:

- Conditions for each days exposure given in Table 8.82.
- Degradation test conditions: 50cc system organic stripped twice (O/A =1) with unused 200 gpl H_2SO_4; stripped organic contacted with copper stock solution, pH = 1.36 for first four tests, pH = 2.0 for last five tests; a second system organic sample contacted same stock solution, i.e., stock solution was contacted twice with two used organic samples, stock pH not adjusted between contacts.

Unused organic same as system organic, 15 % LIX 622, contacted with a 30 gpl Cu, 200 gpl H_2SO_4 solution, then contacted with stock solution as described above for system organic.

TABLE 6.20. LIX 622 LONG TERM EXPOSURE DEGRADATION TEST SUMMARY: LOADING.

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Loading, gpl/% LIX 622	
			System Organic	New Organic
	Stock Aqueous Solution, 3.112 gpl Cu, 3.958 gpl Fe, 0.122 gpl Zn, 2.014 gpl Cr, 6.061 gpl Ni, 0.287 gpl Al, 0.319 gpl Ca			
	First Day			
3478	46.5 liters Aqueous	First	0.203	
3479	" "	Second	0.004	
3480	None	First		0.199
3481	"	Second		0.008
	Second Day			
3495	86.5 liters	First	0.200	
3496	" "	Second	0.005	
3497	None	First		0.205
3496	"	Second		0.014
	Third Day			
3514	125.5 liters	First	0.200	
3515	"	Second	0.006	
3516	None	First		0.205
3517	"	Second		0.001
	Fourth Day			
3536	161.5 liters	First	0.200	
3537	"	Second	0.006	
3540	None	First		0.206
3541	"	Second		0.002

TABLE 6.20. CONTINUED

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Loading, gpl/% LIX 622	
			System Organic	New Organic
	Fifth Day			
3550	187.0 liters	First	0.207	
3551	None	First		0.205
	Sixth Day			
3615	206.5	First	0.205	
3616	"	Second	0.002	
3617	None	First		0.207
3618	"	Second		-
	Seventh Day			
3635	241.0 liters	First	0.200	
3636	"	Second	0.006	
3637	None	First		0.206
3638	"	Second		0.001
	Eighth Day			
3647	275.5 liters	First	0.190	
3648	"	Second	0.016	
3649	None	First		0.204
3650	"	Second		0.003
	Ninth Day			
3665	287.5 liters	First	0.199	
3666	"	Second	> 0.013	
3667	None	First		0.206
3668	"	Second		-

Note: . Conditions for each days exposure presented in Table 8.83.

The leach solutions investigated in the current study contained zinc (5-6 gpl), aluminum (2-3 gpl) and small amounts of cadmium (0.2-0.3 gpl), calcium (0.5 gpl) and iron (0.2-0.5 gpl). The results of detailed experimental studies are presented and discussed in Section 8.7; large scale Phase I testwork (zinc removal after jarosite treatment and Cu SX) is presented in Section 8.13. Large scale and continuous Phase II testwork results (iron removal by SX rather than by jarosite precipitation) are presented in Section 8.4. The experimental procedure is described in Section 5.2.2 and the large scale equipment is shown schematically in Section 5.2.2.2, and pictorally in Section 8.14.2.

6.3.5.1. Large Scale Zinc Solvent Extraction (Phase I)

The results of large scale Phase I testwork are summarized in Table 6.21. Zinc can be effectively extracted by D_2EHPA. An apparent upper limit on the zinc content in the leach solution is 5-6 gpl using a forty volume percent D_2EHPA reagent mixture. Seven cells are required to accomplish effective zinc recovery from the leach solution; four stages of contact; three stages of strip. Solution pH adjustment is required after the first two contacts in order to ensure zinc removal to <70 mg/l.

Iron (Fe^{+3}) is coextracted by D_2EHPA. It is not stripped by sulfuric acid and, therefore, occupies extractant sites in the organic phase. Iron must be removed from the organic or else it will blind up all the sites over a period of time. Iron can be stripped from the organic phase by 4-6 N hydrochloric acid. Therefore, the proposed treatment process consists of: extraction of zinc, residual iron, calcium and aluminum from the leach solution in four stages of pH controlled contact; strip of the zinc from the organic by 200 gpl H_2SO_4 in three stages of contact; removal of an appropriate amount of bleed solution from the sulfuric acid stripped organic; strip the bleed organic phase with 4-6N HCl to remove the Fe^{+3} and Al^{+3}; recycle the bleed organic back to the system organic phase going into the extraction stages. If calcium is present in the leach solution it will be extracted with the zinc and subsequently will be stripped by sulfuric acid in the strip cells. It forms gypsum solid that can be continuously filtered from the aqueous strip phase.

TABLE 6.21. SUMMARY OF LARGE SCALE TESTS ON SOLVENT EXTRACTION OF ZINC WITH D_2EHPA

Sample No.	Condition	Zinc Extraction From Leach Solution		
		Percent	Zinc Content in Solution	
			Initial (gpl)	Final (gpl)
	Sequential Series One (Table 8.86)			
1532	Raffinate From Contact. (25 lit.)	80.5	5.14	1.00
	Sequential Series Three (Table 8.89)			
2109	Raffinate From Contact. (20 lit.)	97.4	5.70	0.15
	Sequential Series Four (Table 8.90)			
2181	Raffinate From Contact. (50 lit.)	97.8	5.89	0.13
2256	Raffinate From Contact. (90 lit.)	98.8	4.94	0.060
	Sequential Series Five (Table 8.91)			
2526B	Raffinate From Contact. (160 lit.)	98.9	6.20	0.070

Note: . Detailed results presented in Section 8.13.

Zinc solvent extraction appears appropriate for selectively removing zinc from a chromium and nickel bearing solution; and for eliminating calcium, iron and aluminum from the leach solution.

6.3.5.2. Zinc Solvent Extraction (Phase II)

As noted previously the major difference in flowsheet testing between Phase I and Phase II was that iron was removed in Phase I testwork by jarosite precipitation with residual iron removal concurrent with zinc solvent extraction. Whereas iron (present at much lower concentrations) was removed in Phase II testwork by solvent extraction.

The results of large scale Phase II testwork are summarized in Table 6.22. The continuous testwork to determine reagent loss rates and potential degradation of reagent are summarized in Table 6.23.

The large scale testwork was conducted in a series of ten cells; one cell for preferentially loading iron; one cell for stripping zinc from the iron loaded organic; three cells for stripping iron loaded organic; three cells for zinc loading; and two cells for stripping zinc loaded organic. Zinc is effectively extracted from the aqueous leach phase, i.e., zinc concentrations in the aqueous phase can be lowered to below 50 ppm without appreciable coextraction of chromium or nickel.

Initially a problem with crud formation was experienced in the iron extraction cell. (This problem is discussed in greater detail in Section 8.4.3.) The solution to the problem was to use a kerosene solvent containing a lower aromatic constituent content. A switch from use of KERMAC 470B to KERMAC 510 solved the crud problem.

Organic loss by carryout from the load circuit into the final raffinate was measured by periodically collecting a liter of raffinate in a graduated cylinder, allowing the organic phase to separate, then measuring the volume of organic per liter of raffinate. The carryout rate ranged from 0.25 cc/l to

TABLE 6.22. SUMMARY OF LARGE SCALE TESTS ON SOLVENT EXTRACTION OF ZINC AND IRON WITH DEHPA (PHASE II)

Sample No.	Condition	Extracted From Leach Solution					
		Content in Solution				Percent	
		Initial(gpl)		Final(gpl)			
		Zn	Fe	Zn	Fe	Zn	Fe
	FIRST DAY,75 lit.						
3281-B	First Cell Feed	1.815	1.164				
3284	Raffinate			0.014	D.L.	99.2	100.0
	SECOND DAY,75 lit.						
3351	First Cell Feed	2.208	1.532				
3328	Raffinate			0.028	0.040	98.7	97.4
	THIRD DAY,75 lit.						
3351	First Cell Feed	2.220	1.891				
3367	Raffinate			0.043	0.010	98.1	99.5
	FOURTH DAY,75 lit.						
3414	First Cell Feed	2.436	2.362				
3454	Raffinate			0.061	0.053	97.5	97.8

Notes: . Test conditions presented in Table 8.48.
. Detailed results presented in Table 8.49.

TABLE 6.23. SUMMARY OF LONG TERM CONTINUOUS TESTWORK: ZINC AND IRON REMOVAL

Sample No.	Condition	Extracted From Leach Solution					
		Content in Solution				Percent	
		Initial(gpl)		Final(gpl)			
		Zn	Fe	Zn	Fe	Zn	Fe
	FIRST DAY, 19 lit.						
3745	First Cell Feed	1.828	2.023				
3787	Final Raffinate			0.080	0.498*	95.6	75.4
	SECOND DAY,19 lit.						
3805	First Cell Feed	0.354	2.276				
3835	Final Raffinate			0.094	0.070	73.4	96.9
	THIRD DAY, 19 lit.						
3846	First Cell Feed	2.207	2.742				
3863	Final Raffinate			0.035	0.027	98.4	99.0
	FOURTH DAY, 19 lit.						
3881	First Cell Feed	2.128	2.035				
3908	Final Raffinate			0.046	0.319*	98.5	84.3
	FIFTH DAY, 19 lit.						
3926	First Cell Feed	1.999	2.218				
3944	Final Raffinate			0.031	0.022	98.4	99.0
	SIXTH DAY, 19 lit.						
3953	First Cell Feed	2.162	2.127				
3969	Final Raffinate			0.050	0.238*	97.7	88.8
	SEVENTH DAY, 19 lit.						
3992	First Cell Feed	2.084	2.299				
4022	Final Raffinate			0.066	0.051	96.8	97.8
	EIGHTH DAY, 19 lit.						
4057	First Cell Feed	1.067	0.582				
4054	Final Raffinate			0.043	0.028	96.0	95.2

TABLE 6.23. CONTINUED

Notes:
- * Iron not completely oxidized.
- Test conditions presented in Table 8.54.
- Detailed results presented in Table 8.53.

0.54 cc/l. These numbers are very dependent on system characteristics. Commercially entrainments range up to several hundred mg/l.

A series of continuous exposure tests were conducted to provide long term degradation data. These tests were conducted in the Bell Engineering testrack. There was no apparent effect of continuous exposure over 38 hours of cumulative exposure, Table 6.24; approximately seven and one-half liters of organic was exposed (one stage of low pH iron loading, three stages of higher pH zinc loading, three stages of zinc stripping, three stages of iron stripping) to 150 liters of aqueous leach solution. Therefore, the aqueous/organic contact ratio was 20 (approximately 58 load/strip cycles).

Detailed experimental results and further discussion are presented in Appendix Section 8.8.2.

6.3.6. Chromium Oxidation

Selective removal of chromium from a mixed metal solution containing iron, copper, zinc, nickel, aluminum does not appear possible without conversion to an oxidized anionic form. To accomplish the oxidation of Cr^{+3} requires a strongly oxidizing environment. This fact means that the oxidation must be performed after any solvent extraction unit operation because strongly oxidizing solutions are expected to degrade the organic extracting reagents(31). Therefore, the most appropriate place in the treatment sequence is after iron, copper and zinc removal. The emphasis, therefore, for this study was placed on treating chromium and nickel bearing solutions. For practically all cases, actual leach solutions pretreated for iron, copper and zinc removal were used for the testwork. The solutions considered in the Phase I study contained approximately 2-6 gpl Cr^{+3}, and 2-5 gpl Ni.

Detailed experimental studies are presented and discussed in Section 8.9.1.; large scale testwork is presented in Section 8.13. The experimental procedure is described in Section 5.3. Large scale chlorine oxidation equipment is presented pictorially in Section 8.14.2.

TABLE 6.24. DEHPA LONG TERM EXPOSURE DEGRADATION TEST

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Loading, gpl (Zn+Fe)/% DEHPA	
			System Organic	New Organic
4025	Stock Aqueous Solution, pH = 2.0, 11.639 gpl Fe, 11.192 gpl Zn			
	First Day			
3841	19 liters aqueous	First	0.257	
3842	" "	Second	0.068	
3843	None	First		0.327
3844	"	Second		0.032
	Second Day			
3874	38 liters	First	0.261	
3875	" "	Second	0.054	
3876	None	First		0.270
3877	"	Second		0.056
	Third Day			
3909	57 liters	First	0.242	
3910	" "	Second	0.066	
3911	None	First		0.286
3912	"	Second		0.051
	Fourth Day			
3947	76 liters	First	0.271	
3948	" "	Second	0.056	

TABLE 6.24. CONTINUED

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Loading, gpl (Zn+Fe)/% DEHPA	
			System Organic	New Organic
3947	None	First		0.259
3948	"	Second		0.068
	Fifth Day			
3982	96 liters	First	0.248	
3983	" "	Second	0.054	
3984	None	First		-
3985	"	Second		-
	Sixth Day			
4026	115 liters	First	0.286	
4027	" "	Second	0.029	
4028	None	First		0.278
4029	"	Second		0.065

Notes: . Detailed experimental results presented in Table 8.95.

A relatively large number of oxidation possibilities were considered. Only two oxidation techniques are considered feasible because of reagent cost. They are chlorine oxidation and electrochemical oxidation.

Large scale testwork using chlorine oxidation showed that slurry oxidation of precipitated chromium was effective and controllable. The operational procedure consisted of adjusting the solution pH to 4-5 (thereby precipitating most of the Cr^{+3} as $Cr(OH)_3$); sparging in Cl_2 gas to raise the solution Eh to >1,000 mv; and then allowing the reaction to proceed for several hours. Eighty to ninety five percent of the chromium was oxidized to the dichromate form. The unoxidized $Cr(OH)_3$ solid can either be separated from the solution and recycled to the leach stage or left in the reactor to become a part of the next oxidation treatment.

The oxidation time period used to treat large volumes was relatively long in the large scale testwork. However, short time exposures were effective in the small-scale testwork. The reason for the difference was the effectiveness of the contact system used. A more appropriately designed reactor was tested in the Phase II study, but the results did not show an improvement in the oxidation rate, Section 8.9.1.1.2.

Oxidation of chromium achieved by chlorine sparging was in the range 70-80% for a contact period of 4-5 hours at a pH of 4-5; the oxidation achieved by use of an aspirating chlorinator was in range 40-70% for a contact period of 4-5 hours at a pH of 4-5. Complete oxidation is not, however, required because the solid residue contains the reoxidized chromium as chromium hydroxide. It is not lost from the system but is recycled to the initial leach unit operation. The filtrate solution from the solid/liquid separation (that is further treated for chromium recovery) is essentially chromium anions, e.g., 99% Cr^{+6} (as an anion), 1% Cr^{+3}.

Electrochemical oxidation is commercially practiced for regenerating spent plating baths(32,33). The cell electrodes are separated by a cation permeable membrane. Chromium is oxidized in the anode compartment and impurities in the anolyte transport across the membrane to the catholyte. This system appears to be applicable to the present treatment sequence; chromium could be oxidized and copper could be removed from the copper SX strip acid. The operational procedure would be: pump the leach solution into the anode chamber for chromium oxidation; pump the copper bearing strip solution from the copper SX strip cells into the cathode chamber for copper extraction; recycle the copper depleted strip solution to the copper SX strip cells to pick up more copper; pump the oxidized leach solution on to chromium recovery. Some nickel would transport from the leach solution to the cathode chamber through the membrane but it would not interfere with either the copper electrowinning process or the copper SX stripping process. When the nickel content built up to an appreciable level a bleed stream ($\sim$10%) from the copper SX strip stream would be pulled off for nickel recovery. Nickel could be recovered by recycling the solution to the initial leach stage.

Electrochemical oxidation has been investigated on a small-scale basis in the Phase I study. The results are presented and discussed in Section 8.9.1.2.1. The results were encouraging so large-scale testwork was conducted during the Phase II study.

The electrooxidation cell was described previously in Section 5.3.2. The cell consisted of two box chambers capable of treating about 14 liters of anolyte and 26 liters of catholyte in a batch or continuous flow mode. Experimental testwork is summarized in Table 6.25. Detailed experimental testwork results and discussion of results are presented in Section 8.9.1.2. Steady state conditions produced oxidation conversion of between 80-95 percent of the chromium. The testwork supports the conclusion that electrochemical oxidation is a potential unit operation to be considered further.

6.3.7. Chromium Precipitation

A very effective procedure has been developed to selectively strip the oxidized chromium from the solution nickel. The procedure is based on the relative solubility of lead sulfate and lead chromate. The procedure consists of: exposing the oxidized chromium bearing solution to solid lead sulfate in

TABLE 6.25 SUMMARY OF CONTINUOUS ELECTROCHEMICAL OXIDATION OF CHROMIUM

Sample No.	Condition	Chromium Oxidation (%)
5003	Batch Test	85.4
5006	Series One Test (Table 8.105)	78.0
5013	Series Two Test (Table 8.106)	87.2
5039	Series Three Test (Table 8.107)	95.6

Notes: . Test conditions presented in above referenced tables in Section 8.9.1.2.

the pH range 4-5; lead chromate forms as a dense, crystalline precipitate; the solids are allowed to settle and the chromium free (<7mg/l Cr) solution is pumped away from the settled solids; the remaining slurry is recontacted with more oxidized chromium bearing solution and the process repeated. The exchange reaction is complete in a few minutes time. The lead sulfate can be regenerated and the chromium recovered in a concentrated form by leaching the solids in sulfuric acid. The regenerated lead sulfate is then recycled to the precipitation vessel.

The basis for the precipitation process is shown in Figure 6.6. The diagram shows that $PbCrO_4$ (solid lines on the diagram) is the stable phase above pH levels of: 2 for $SO_4/Cr = 1$; 2.8 for $SO_4/Cr = 10$; and 3.7 for $SO_4/Cr = 100$. Therefore, the pH range of 4-5 is appropriate for all the test conditions used in the present study to produce $PbCrO_6$. It also demonstrates that the redissolution of $PbCrO_4$ can be achieved at pH levels below the intersection between the dashed and solid lines, i.e., for a $SO_4/Cr = 1$ a pH <2 will convert the $PbCrO_4$ to $PbSO_4$.

The detailed experimental results are presented in Section 8.10.1.1; large-scale sequential testwork in Section 8.13. The large-scale test results are summarized in Table 6.26.

6.3.8. Nickel Precipitation

Nickel sulfide can be effectively precipitated from a nickel bearing solution by the addition of a sodium sulfide solution. If the sulfide solution is added at the proper concentration and rate there is no release of hydrogen sulfide gas. The precipitation is performed on the solution resulting from the removal of chromium, which is at a pH of 4-4.5. Precipitation of nickel from a solution at this pH value results in effective nickel removal, e.g., large-scale testwork showed the following results. Nickel was decreased from 2.27 gpl in 3.5 liters of sequentially treated leach solution to 7 mg/liter. Nickel was decreased from 1.67 gpl in 42 liters of sequentially treated leach solution to 6 mg/liter.

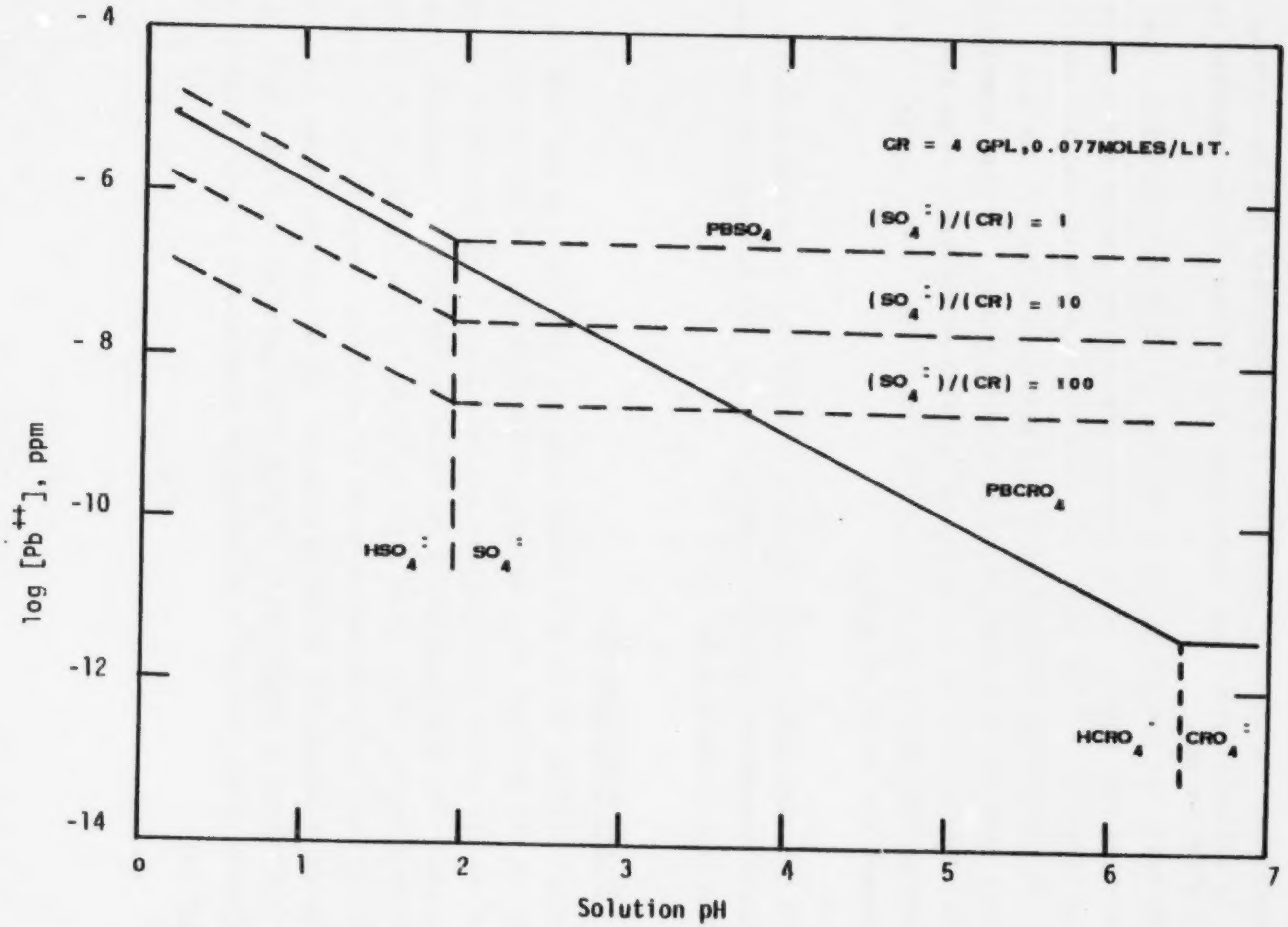


Figure 6.6. Lead chromate-lead sulfate stability diagram.

TABLE 6.26. SUMMARY OF LARGE SCALE TESTS ON CHROMIUM PRECIPITATION

Sample No.	Condition	Chromium Removed From Solution		
		Percent	Chromium Content In Solution	
			Initial (gpl)	Final (gpl)
	Sequential Series Four (Table 8.90)			
2347	Starting Solution (10 liters)	-	1.65	-
2376	Final Filtrate after 30 min. exposure	99.5	-	0.008
	Sequential Series Five (Table 8.91)			
2600	Starting Solution (42 liters)	-	2.34	-
2602	Final Filtrate after 30 min. exposure	99.7	-	0.007

Note: . Detailed experimental results presented in Section 8.13.

The precipitation is rapid and complete in less than one-half hour. Therefore, a relatively small reaction vessel is appropriate for the precipitation. A deficiency of sodium sulfide should be used so that solution sulfide ions do not exist. Otherwise hydrogen sulfide would be generated when this solution is recycled to the leach unit operation.

The detailed experimental results are presented in Section 8.11.1.; large scale testwork in Section 8.13. Alternate nickel recovery possibilities are presented in Section 8.11.2 and 8.15.7.4.

6.4. ECONOMIC ANALYSIS

The following cost summary is presented as a first order estimate(49,50) for the flowsheet presented in Figure 6.7. Itemized equipment lists were used where possible and literature quoted cost figures were used when available. Costs were estimated using the data of Mular(49), Word(50), and Davenport(39). All costs have been updated to second quarter 1984 using the Marshall and Stevens (M&S) Index. The current M&S Index value is 794. Major cost items have been included. The factored capital cost totals take care of minor equipment, instrumentation, processing piping, auxiliary engineering cost, and plant size factor. Detailed cost sheets, both for capital and operating costs, are presented in Appendix 8.15.

This is certainly not a detailed engineering cost analysis. It is only what Mular and Davenport claim for the calculational technique, i.e., a first order estimate. Mular suggests that the cost totals will be within ±30 percent. If cost were not available for the present flowsheet individual unit operation capacity but data existed for a similar commercial unit operation the sixth tenth rule was used, i.e.,

$$\text{cost} = \text{cost}_{\text{known}}[\text{capacity}_{\text{present}}/\text{capacity}_{\text{known}}]^{0.6}(\text{M\&S}_{\text{now}}/\text{M\&S}_{\text{then}})$$

The potential value of products(47) and reagent costs were obtained from current literature quotations and are reported in Tables 6.27 and 6.28.

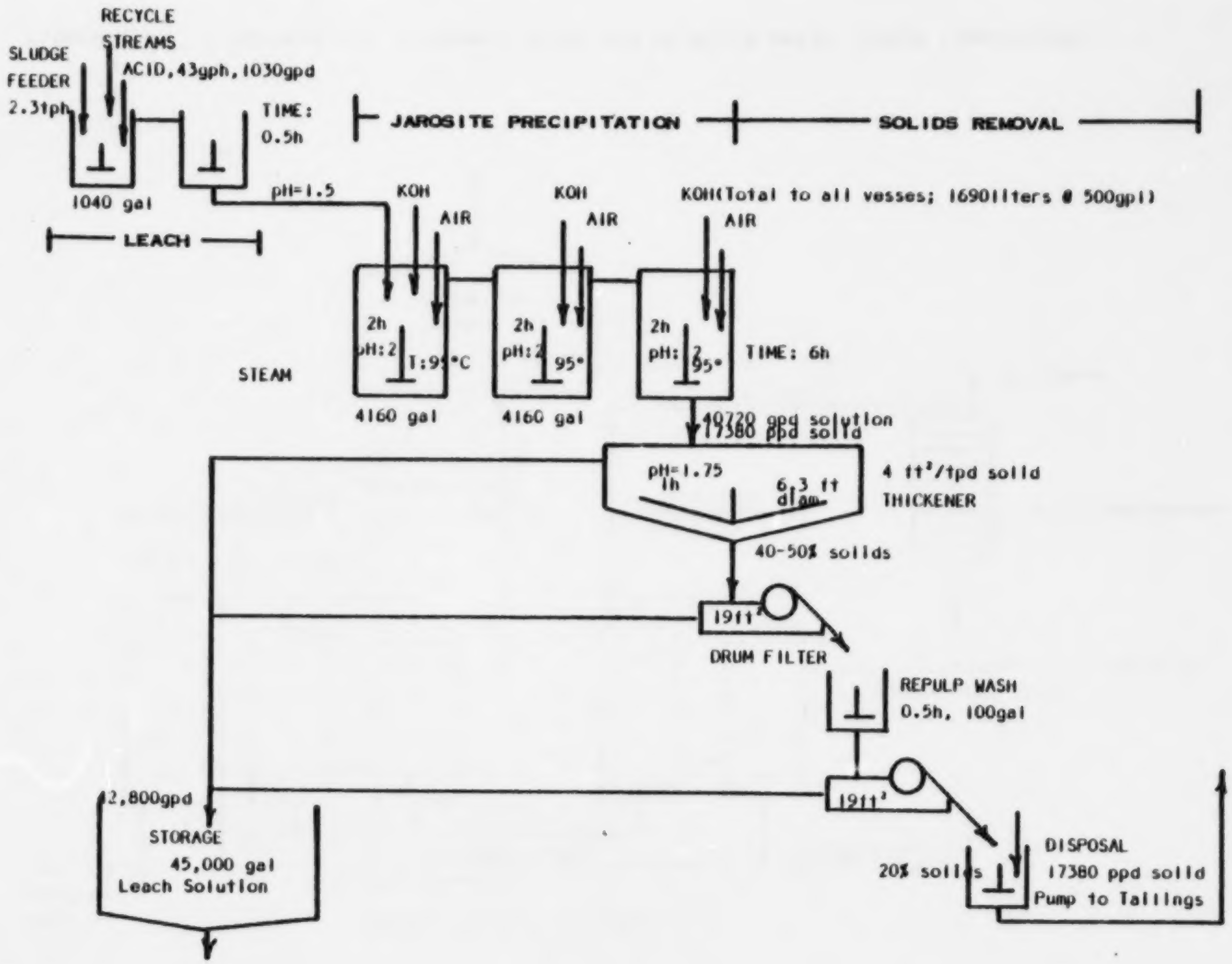

RECYCLE STREAMS
SLUDGE FEEDER 2.3tph
ACID, 43gph, 1030gpd
TIME: 0.5h
1040 gal
LEACH
JAROSITE PRECIPITATION
SOLIDS REMOVAL
pH=1.5
KOH
AIR
KOH
AIR
KOH(Total to all vesses; 1690liters @ 500gpl)
AIR
2h
pH:2
T:95°C
2h
pH:2
95°
2h
pH:2
95°
TIME: 6h
STEAM
4160 gal
4160 gal
40720 gpd solution
17380 ppd solid
pH=1.75
1h
6.3 ft diam
4 ft²/tpd solid
THICKENER
40-50% solids
19ft²
DRUM FILTER
REPULP WASH
0.5h, 100gal
19ft²
2,800gpd
STORAGE
45,000 gal
Leach Solution
DISPOSAL
17380 ppd solid
Pump to Tailings
20% solids

Figure 6.7. Flowsheet for treatment of 50 tpd of mixed metal sludge.

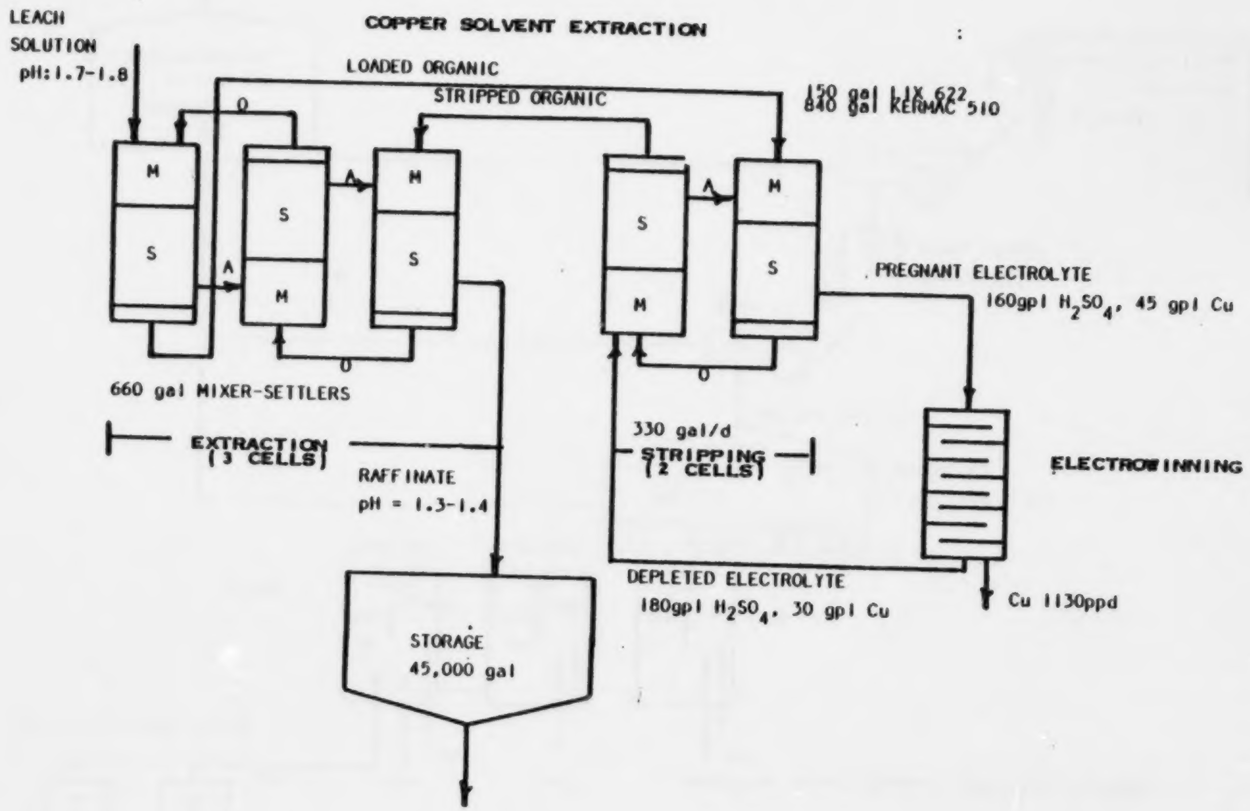

COPPER SOLVENT EXTRACTION
LEACH SOLUTION pH:1.7-1.8
LOADED ORGANIC
STRIPPED ORGANIC
150 gal LIX 622
840 gal KERMAC 510
M
S
A
O
660 gal MIXER-SETTLERS
EXTRACTION (3 CELLS)
RAFFINATE pH = 1.3-1.4
STORAGE 45,000 gal
330 gal/d
STRIPPING (2 CELLS)
PREGNANT ELECTROLYTE
160gpl H_2SO_4, 45 gpl Cu
ELECTROWINNING
DEPLETED ELECTROLYTE
180gpl H_2SO_4, 30 gpl Cu
Cu 1130ppd

Figure 6.7. Flowsheet for treatment of 50 tpd of mixed metal sludge (continued).

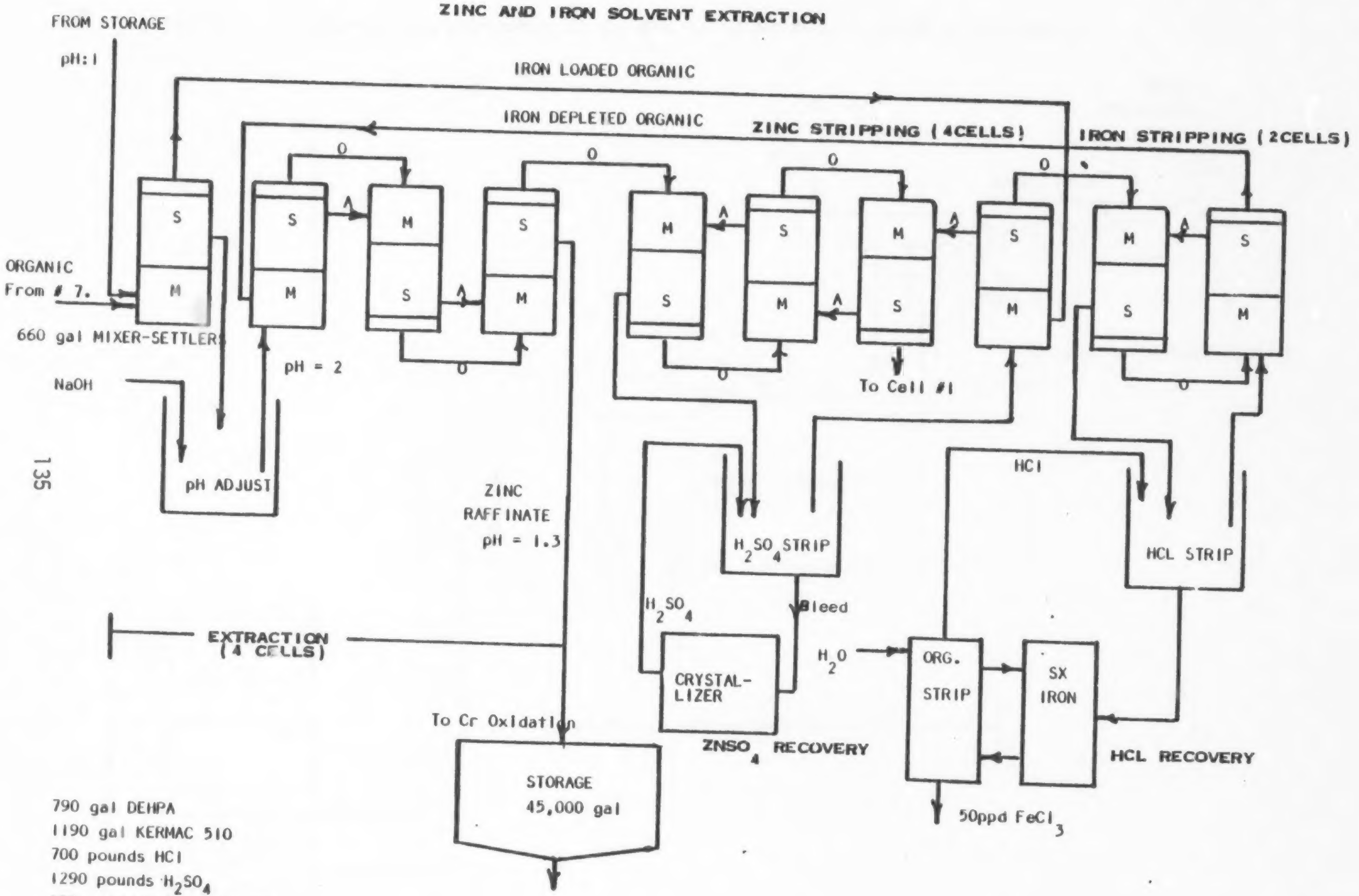

ZINC AND IRON SOLVENT EXTRACTION
FROM STORAGE
pH: 1
IRON LOADED ORGANIC
IRON DEPLETED ORGANIC
ZINC STRIPPING (4CELLS)
IRON STRIPPING (2CELLS)
ORGANIC
From # 7.
660 gal MIXER-SETTLERS
S
M
O
A
pH = 2
NaOH
pH ADJUST
To Cell #1
ZINC
RAFFINATE
pH = 1.3
H_2SO_4 STRIP
Bleed
H_2SO_4
CRYSTAL-
LIZER
$ZNSO_4$ RECOVERY
HCl
HCL STRIP
H_2O
ORG.
STRIP
SX
IRON
HCL RECOVERY
50ppd $FeCl_3$
EXTRACTION
(4 CELLS)
To Cr Oxidation
STORAGE
45,000 gal
790 gal DEHPA
1190 gal KERMAC 510
700 pounds HCl
1290 pounds H_2SO_4
105 gal/d NaOH, 500 gpl

Figure 6.7. Flowsheet for treatment of 50 tpd of mixed metal sludge (continued).

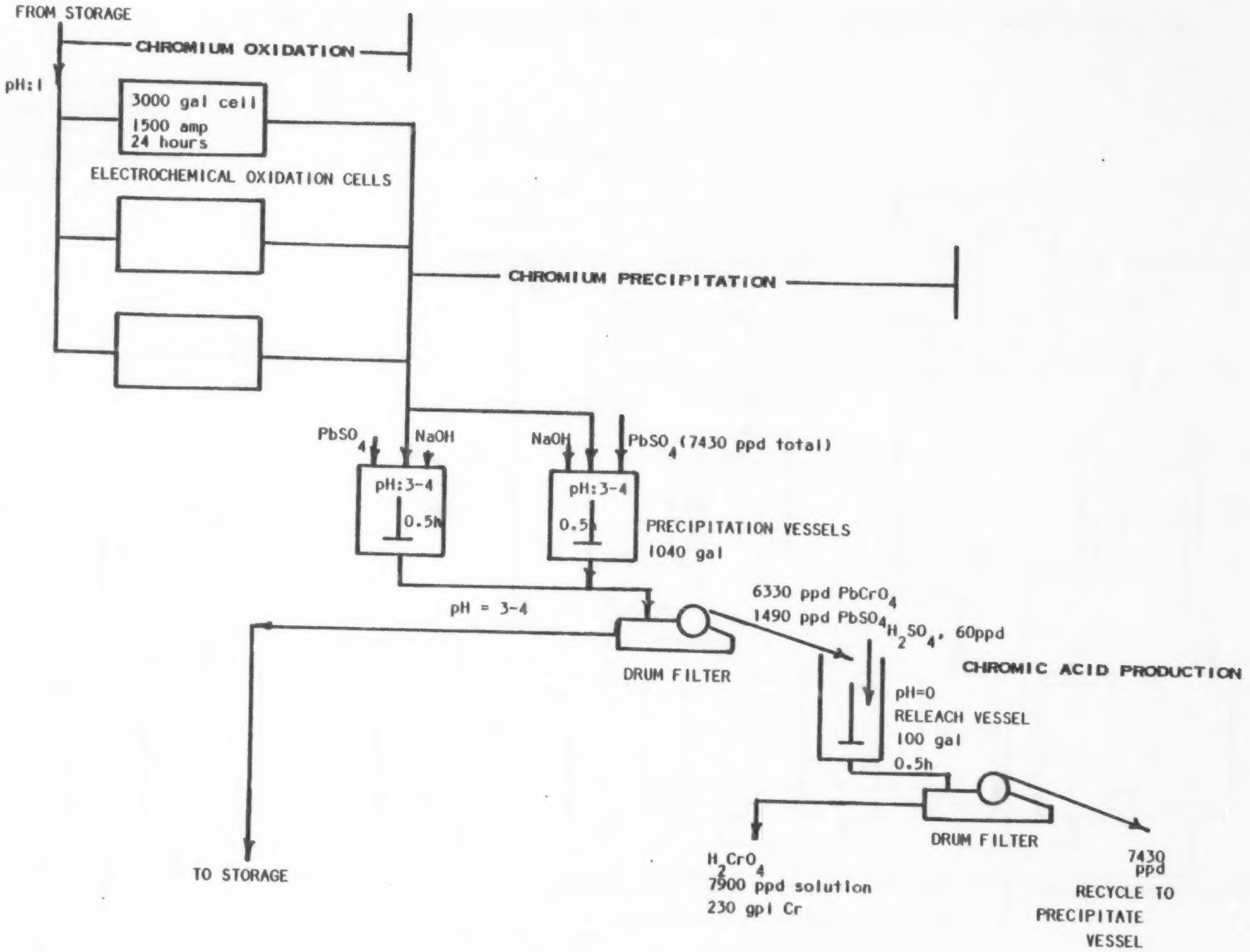

FROM STORAGE
CHROMIUM OXIDATION
pH:1
3000 gal cell
1500 amp
24 hours
ELECTROCHEMICAL OXIDATION CELLS
CHROMIUM PRECIPITATION
PbSO4
NaOH
NaOH
PbSO4 (7430 ppd total)
pH:3-4
0.5h
pH:3-4
0.5h
PRECIPITATION VESSELS
1040 gal
pH = 3-4
6330 ppd PbCrO4
1490 ppd PbSO4
H2SO4, 60ppd
DRUM FILTER
CHROMIC ACID PRODUCTION
pH=0
RELEACH VESSEL
100 gal
0.5h
TO STORAGE
DRUM FILTER
H2CrO4
7900 ppd solution
230 gpl Cr
7430 ppd
RECYCLE TO
PRECIPITATE
VESSEL

Figure 6.7. Flowsheet for treatment of 50 tpd of mixed metal sludge (continued).

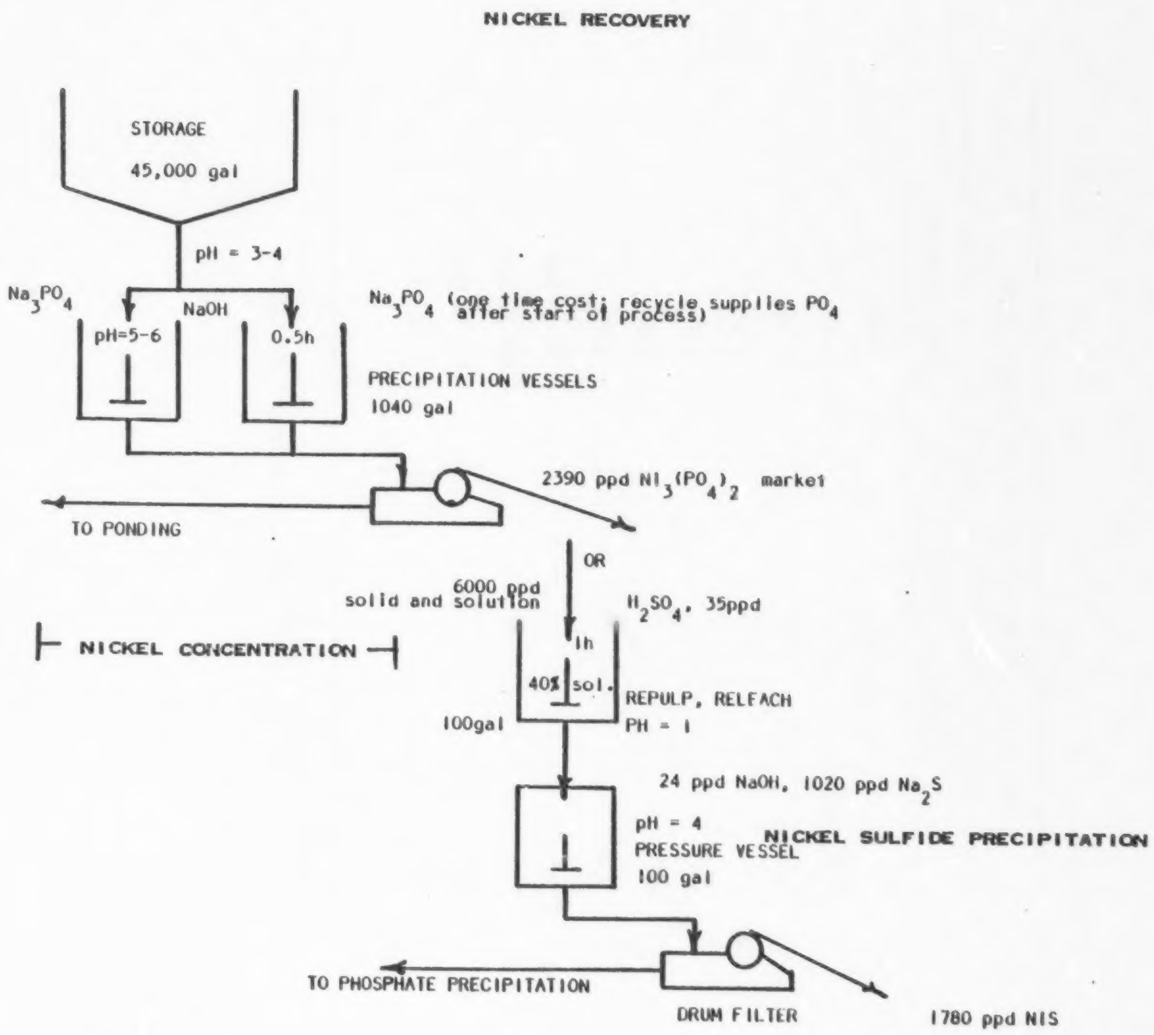

NICKEL RECOVERY
STORAGE
45,000 gal
pH = 3-4
Na3PO4
NaOH
pH=5-6
0.5h
Na3PO4 (one time cost; recycle supplies PO4 after start of process)
PRECIPITATION VESSELS
1040 gal
2390 ppd Ni3(PO4)2 market
TO PONDING
OR
6000 ppd solid and solution
H2SO4, 35ppd
NICKEL CONCENTRATION
1h
40% sol.
REPULP, RELEACH
PH = 1
100gal
24 ppd NaOH, 1020 ppd Na2S
pH = 4
PRESSURE VESSEL
100 gal
NICKEL SULFIDE PRECIPITATION
TO PHOSPHATE PRECIPITATION
DRUM FILTER
1780 ppd NiS

Figure 6.7. Flowsheet for treatment of 50 tpd of mixed metal sludge (continued).

TABLE 6.27. VALUE OF PRODUCTS AND REAGENT COSTS

Product	Cost ($/pound)
Cu	0.60
$ZnSO_4 \cdot H_2O$	0.20
H_2CrO_4	1.18
Ni	3.45
NiS	1.72
NiO	2.60
$PbSO_4$	0.85
H_2SO_4	60 ($/ton)
NaOH	300 ($/ton)
Na_2S	470 ($/ton)
Cr_2O_3	1.90

Sources: October Issue EMJ
Chemical Market Reporter, September 17, 1984.

TABLE 6.28. TOTAL PRODUCT VALUE FOR 50 TPD COST ESTIMATE

Product	Quantity (pounds/day)	Potential Value ($/Yr)
1. Cu	1130	223,700
2. $ZnSO_4 \cdot H_2O$	3180	209,900
3. H_2CrO_4	2310	899,500
4. NiS	1780	1,010,300
5. Ni	1150	1,309,300
6. Cr_2O_3	1490	934,200
7. NiO	1460	1,252,700
8. Credit for Disposal ($1/gallon sludge)*		3,300,000
	TOTAL (1,2,3,4,8)	5,643,400
	TOTAL (1,2,3,7,8)	5,885,800
	TOTAL (1,2,5,6,8)	5,977,100

---

*Disposal costs vary considerably depending on amount of material that must be handled.

The return on investment (ROI) was calculated by the equation:

$$\text{ROI} = \frac{(\text{Value of Products-Annualized Cost})(\text{tax rate})(100)}{\text{Capital Cost}}$$

The cost estimate is based on the flowsheet presented in Figure 6.7. Capital cost and operating cost were estimated. These estimates are presented in Appendix Section 8.15. Equipment costs were based on cost equations of the form:

$$\text{cost}_{\text{now}} = a(\text{capacity})^{b}(\text{M\&S}_{\text{now}}/\text{M\&S}_{\text{then}})$$

where a, b are constants for a particular piece of equipment. The constants a and b are provided for a variety of types of equipment by Mular, Woods, and Davenport (and in some cases on other literature data).

An equipment list was prepared for each series of unit operations, the cost estimated as described above. The Factored Capital Cost was determined by using the factors as presented in Table 6.29. An annualized cost was then determined based on a five year period, 12 percent interest rate. An operational cost for the series of unit operations was established based on reagent consumption, manpower requirements, maintenance and power consumption. The results of the calculations are presented in Tables 8.131-8.145.

Operating cost estimates are presented in Table 8.131. The operating cost estimates do not include personnel other than operational personnel. The estimates include: unit operations cost; manpower requirements; maintenance costs; and energy cost.

The ROI calculations were made based on the following assumptions: buildings and land are available; tax rate is 50 percent; interest rate is 12 percent; pay-off period is five years; a credit of one dollar per gallon of sludge is allowed; and the plant operates for 330 days per year. The quantity of material to be treated is based on 50 tpd sludge containing 25 weight percent solids. The solids contain five weight percent of each element, Cu,

TABLE 6.29. FACTORED CAPITAL COST ESTIMATE*

	Cost (M&S = 794)
1. Purchased Equipment Costs	
2. Installed Equipment Costs (1.4 x Item 1)	
3. Process Piping (30% of 2)	
4. Instrumentation (10% of 2)	
5. Auxiliaries (5% of 2)	
6. Outside Lines (5% of 2)	
7. Total Physical Plant Costs (Sum of 2 through 6)	
8. Engineering and Construction (20% of 7)	
9. Contingencies (15% of 7)	
10. Size Factor (Small Commercial, 10% of 7)	
11. TOTAL PLANT FIXED CAPITAL COST (Sum of 7 through 10)	
YEARLY COST, Based on 60 month pay-off period, 12% interest	

*Example Estimate Form

Zn, Cr, Ni, seven and one-half percent Fe; two percent Al and P; and one percent Ca. Mass balances were based on actual experimental data generated during this study. The mass balance results were used to size the necessary equipment and are reported in Section 8.15.

The first order estimate return on investment, based on the flowsheet presented in Figure 6.7, and Tables 6.30, 6.31, is 41±12%

$$\mathrm{ROI} = \left(\frac{5{,}643{,}400-2{,}434{,}100}{3{,}868{,}800}\right)(.5)(100) = 41\pm12\%$$

The oxidation unit operation is a major cost in the overall project cost; both for capital and for operating expense. It is expected that significantly lower cost would result using newer technology presently being commercialized. INCO(42) has developed a technology based on the use of sulfur dioxide and oxygen that they are commercializing for cyanide destruction. However, their research results show solution potentials that are sufficiently oxidizing to oxidize chromium. In the case where chromium (+3) and nickel (+2) are present it may be possible at a pH in the basic regions ($\mathrm{pH} \sim 8$) to oxidize a slurry of chromium (+3) hydroxide and nickel (+2) hydroxide to chromate ($CrO_4^{=}$) and solid nickel (+3) hydroxide. Therefore, a separation between chromium and nickel may be possible at a much lower cost than either electrochemical oxidation or chlorine oxidation. This technology was not being used industrially when the present investigations were begun, therefore, it has not been experimentally investigated in this study.

Application of the SO_2-O_2 process to chromium oxidation has not been made and, therefore, costs are not available. However, a first order cost analysis can be made by assuming the chromium oxidation rate will be similar to the measured nickel oxidation rate and by costing out the equipment required to achieve the oxidation. The anticipated unit operations are depicted in Figure 6.8a. An equipment list is presented in Table 8.143; a factored capital cost summary is presented in Table 8.144; operating cost is presented in Table 8.145. The solution oxidizing potential certainly would be great enough to insure thermodynamic oxidation. The kinetics of such a rection, of course, are unknown.

TABLE 6.30 PROCESS COST: FIRST ORDER ESTIMATE

Unit Operation	COST ($)			
	Factored Capital Cost Estimate	Annualized Capital Cost	Operation Cost Per Year	Total Cost Per Year
1. Leach, jarosite precipitation	430,800	119,500	223,500	343,000
2. Jarosite storage	390,500	108,200	25,400	133,600
3. Copper solvent extraction, electro-winning	336,100	93,100	205,900	299,000
4. Zinc, residual iron solvent extraction, zinc sulfate crystallization	661,600	183,300	269,700	453,000
5. Chromium oxid., chromic acid production	1,818,200	503,600	407,700	911,300
6. Nickel recovery	231,600	64,200	230,000	294,200
TOTAL COST	3,868,800	1,071,900	1,362,200	2,434,100

See Section 8.15 for details.

TABLE 6.31 PROCESS COST SUMMARY: FIRST ORDER ESTIMATE

Unit Operation	COST ($)						
	Factored Capital Cost/Yr @ 12%		Operation Cost Per Yr		Total Cost Per Yr		Potential Value of Product(¢/lb)
	$	¢/lb	$	¢/lb	$	¢/lb	
1. Leach, jarosite precipitation	227,700	4.0*	248,900	4.4*	476,600	8.4*	-
2. Copper SX, EW	93,100	25.0	205,900	55.2	299,000	80.2	60
3. Zinc, residual iron SX, zinc sulfate crystallization	183,300	17.4	269,700	25.7	453,000	43.0	20
4. Chromium oxid., chromic acid production	503,600	66.1	407,700	53.5	911,300	119.6	118
5. Nickel recovery	64,200	10.9	230,000	39.0	294,200	49.9	172

* per pound of residue solids.

See Section 8.15 for details.

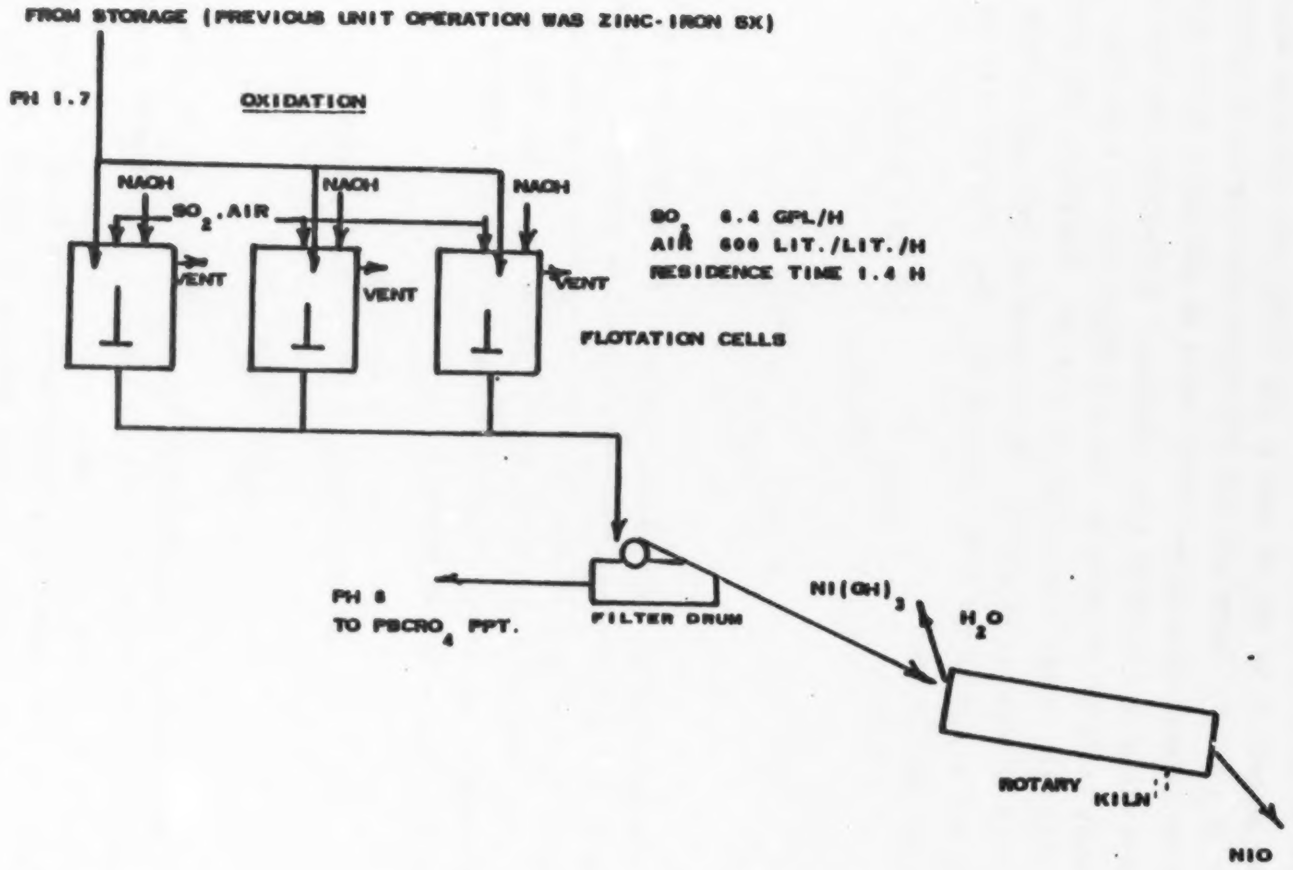

FROM STORAGE (PREVIOUS UNIT OPERATION WAS ZINC-IRON SX)
PH 1.7
OXIDATION
NAOH
NAOH
NAOH
SO2.AIR
VENT
VENT
VENT
SO2 6.4 GPL/H
AIR 600 LIT./LIT./H
RESIDENCE TIME 1.4 H
FLOTATION CELLS
PH 8
TO PBCRO4 PPT.
FILTER DRUM
NI(OH)3
H2O
ROTARY KILN
NIO

Figure 6.8a. SO_2/O_2 oxidation applied to chromium oxidation and nickel recovery.

The proposed possible application to the present system is concurrent oxidation of chromium (+3) and nickel (+2). The chromium (+6) formed ($CrO_4^{=}$) would be present as an aqueous specie; the nickel (+3) hydroxide would be present as a solid. Therefore, not only would the chromium be oxidized but a separation between chromium and nickel would be achieved. In the present flowsheet nickel and chromium exist together. A treatment sequence could be concurrent oxidation of chromium (+3) and nickel (+2) at a pH of $\sim$8. Chromium and nickel will be solid hydroxides at this pH. Therefore, the oxidation would occur in a solid-solution slurry. The research at INCO used calcium sulfite ($CaSO_3$) and oxygen as the oxidizing species. They proposed that the nickel oxidation reaction was:

$$Ni(OH)_{2(solid)} + CaSO_{3(solid)} + 5/2\ H_2O + 3.4\ O_2 \longrightarrow$$

$$Ni(OH)_{3(solid)} + CaSO_4 \cdot H_2O$$

The oxidation was carried out in a modified flotation cell so that good agitation and gas-solid-solution contact could be achieved. The measured oxidation rate was approximately 5 g Ni^{++}/liter/hour at an equivalent SO_2 rate of 7 g SO_2/liter/hour at a pH of 8; Ni^{++} concentration was 13.5 gpl, and an oxygen supply rate of 600 liters/liter/hour was used. A similar chromium oxidation reaction may be possible:

$$Cr(OH)_3 + CaSO_3 + 3/2\ H_2O + 5/4\ O_2 \longrightarrow$$

$$H_2CrO_4 + CaSO_4 \cdot 2H_2O$$

Replacement of the electrochemical oxidation by SO_2-O_2 oxidation and the production of NiO rather than NiS results in a considerable potential cost savings. The process cost is summarized in Table 6.32a. A comparison of costs between the two flowsheets is presented in Table 6.33a. The ROI is 41% for the electrochemical oxidation flowsheet compared to 69% for the SO_2-O_2 modified flowsheet.

TABLE 6.32a. PROCESS COST: FIRST ORDER ESTIMATE MODIFIED FLOWSHEET INCLUDING SO_2-O_2 CHROMIUM OXIDATION

Unit Operation	COST ($)			
	Factored Capital Cost Estimate	Annualized Capital Cost	Operation Cost Per Year	Total Cost Per Year
1. Leach, jarosite precipitation	430,800	119,500	223,000	343,000
2. Jarosite storage	390,500	108,200	25,400	133,600
3. Copper solvent extraction, electrowinning	336,100	93,100	205,900	299,000
4. Zinc, residual iron solvent extraction, zinc sulfate crystallization	661,600	183,300	269,700	453,000
5. Chromium oxidation, chromic acid production, nickel oxide production	1,043,900	289,200	484,600	773,800
TOTAL COST	2,862,900	793,300	1,209,100	2,002,400

TABLE 6.33a. COMPARSION OF FIRST ORDER COST ESTIMATES BETWEEN FLOWSHEETS FOR ELECTROCHEMICAL OXIDATION AND SO_2/O_2 OXIDATION OF CHROMIUM.

Flowsheet	COST ($)				
	F.C.C.	F.C.A.C.	Operating Cost/yr	Total Cost/yr	Product Value*
Electrochemical (Table 2.1)	3,868,800	1,071,900	1,362,200	2,434,100	5,643,400
Modified	2,862,900	793,300	1,209,100	2,002,400	5,885,800

$$\text{R.O.I.} = \left[(5{,}885{,}800 - 2{,}002{,}400)/\ 2{,}862{,}900\right](0.50)(100)$$
$$= 69 \pm 20\ \%$$

* Same products in both flowsheets except for nickel: NiS in Table 2.1, NiO in modified flowsheet.

See Section 6.4 for details.

Another alternative that appears to be attractive is presented in Section 8.15.7.4, solvent extraction of nickel by LIX63-D_2EHPA mixtures, electrowinning nickel, precipitation of chromium hydroxide, production of chromium oxide. The anticipated unit operations are depicted in Figure 6.8b.

The solvent extraction of nickel from leach solutions containing chromium appears to be possible by either use of a LIX63-D_2EHPA organic or a D_2EHPA-EHO organic(44). Preliminary shake tests were performed in this study. The results were encouraging and verified literature data. Certainly further research is needed to verify the conditions needed for an industrial SX system. Also, one should be aware that solvent extraction of nickel using these reagents is more risky than previously suggested alternatives because solvent extraction of nickel (at low pH levels) is not yet practiced commercially.

The data on which the cost estimate for the modified flowsheet (Figure 6.7b) is made are presented in Tables 8.145 and 8.146. The process cost summary is presented in Table 6.32b, and a comparison to the electrochemical oxidation flowsheet is presented in Table 6.33b. The ROI is 41% for the electrochemical oxidation flowsheet compared to 67% for the modified flowsheet. Additional alternative unit operations are discussed in Section 8.15. The two alternate unit operations presented in this section show good potential for an excellent return on investment. Even if a credit is not taken for disposal the modified flowsheets cost estimates show that the treatment process results in income sufficient to offset the cost. It is recommended that further consideration be given to these two flowsheets.

6.5. COMPUTER ASSISTED MASS BALANCE CALCULATIONS

6.5.1. Background

Rapidly escalating costs and constantly declining ore grades have prompted the energy intensive metallurgical industry to seek new ways to improve process economics. One of the methods that could be employed to immediately gain greater operating efficiency could be the modernization of existing plants with

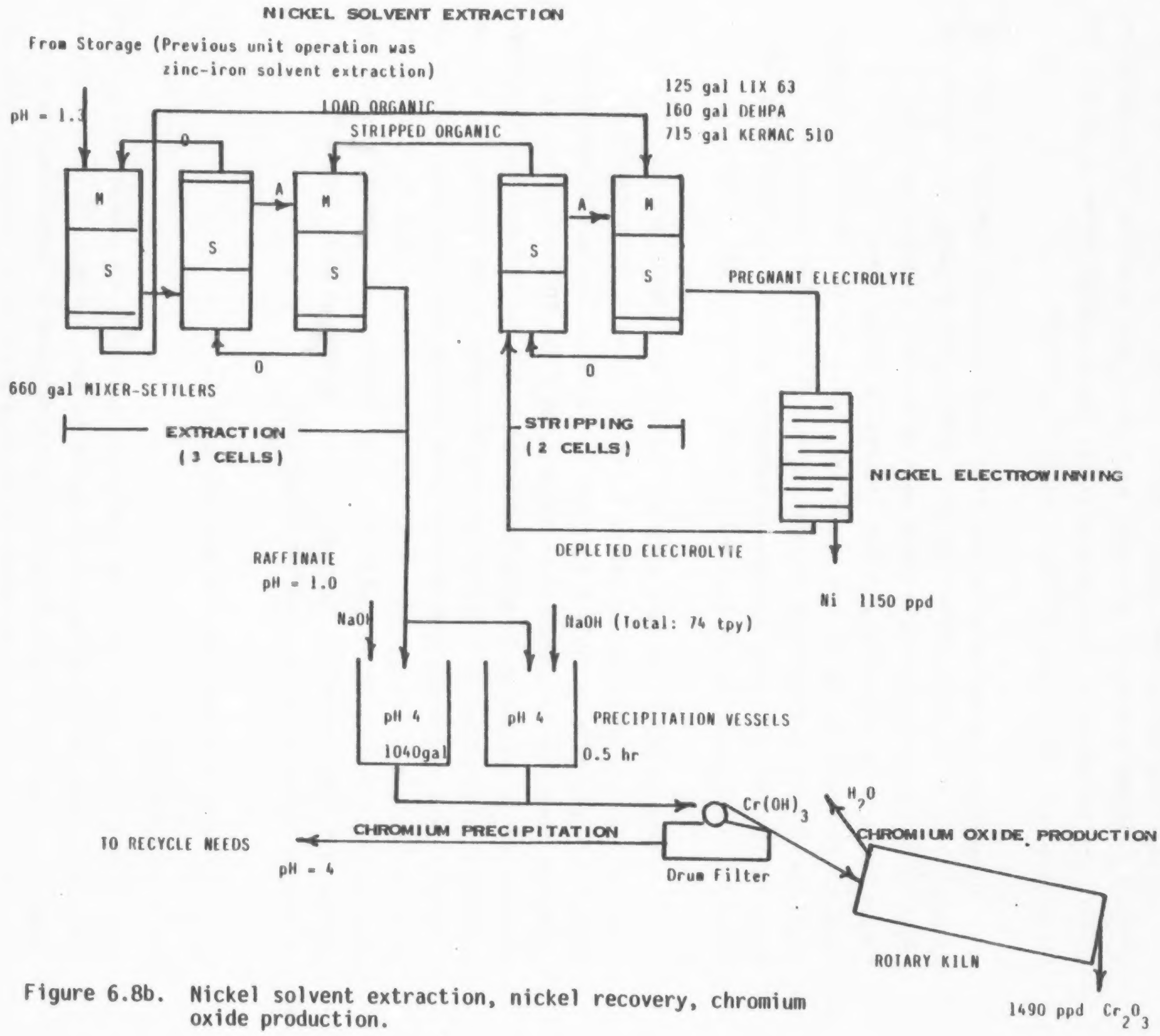

NICKEL SOLVENT EXTRACTION
From Storage (Previous unit operation was zinc-iron solvent extraction)
pH = 1.3
LOAD ORGANIC
STRIPPED ORGANIC
125 gal LIX 63
160 gal DEHPA
715 gal KERMAC 510
M
S
S
A
M
S
S
A
M
S
O
O
O
PREGNANT ELECTROLYTE
660 gal MIXER-SETTLERS
EXTRACTION
(3 CELLS)
STRIPPING
(2 CELLS)
NICKEL ELECTROWINNING
DEPLETED ELECTROLYTE
RAFFINATE
pH = 1.0
Ni 1150 ppd
NaOH
NaOH (Total: 74 tpy)
pH 4
1040gal
pH 4
PRECIPITATION VESSELS
0.5 hr
Cr(OH)3
H2O
CHROMIUM PRECIPITATION
CHROMIUM OXIDE PRODUCTION
TO RECYCLE NEEDS
pH = 4
Drum Filter
ROTARY KILN
1490 ppd Cr2O3

Figure 6.8b. Nickel solvent extraction, nickel recovery, chromium oxide production.

TABLE 6.32b PROCESS COST: FIRST ORDER ESTIMATE MODIFIED FLOWSHEET INCLUDING NICKEL SOLVENT EXTRACTION, NICKEL RECOVERY, AND CHROMIUM OXIDE PRODUCTION

Unit Operation	COST ($)			
	F.C.C.	FCAC	Operating Cost Per Year	Total Cost Per Year
1. Leach, jarosite precipitation	430,800	119,500	223,000	343,000
2. Jarosite ponding	390,500	108,200	25,400	133,600
3. Copper solvent extraction, electrowinning	336,100	93,100	205,900	299,000
4. Zinc, residual iron solvent extraction, zinc sulfate crystallization	661,600	183,300	269,700	453,000
5. Nickel solvent extraction, electrowinning, chromium oxide production	1,158,300	320,800	451,500	772,300
TOTAL COST	2,977,300	824,900	1,175,500	2,000,900

See Section 8.15 for details.

TABLE 6.33b COMPARSION OF FIRST ORDER COST ESTIMATES BETWEEN FLOWSHEETS FOR ELECTROCHEMICAL OXIDATION AND NICKEL SOLVENT EXTRACTION AND RECOVERY.

Flowsheet	FCC	FCAC	Operating Cost Per Year	Total Cost Per Year	Product Value*
Electrochemical	3,868,800	1,071,900	1,362,200	2,434,100	5,643,400
Modified	2,977,300	824,900	1,175,500	2,000,900	5,977,100

$$\text{ROI} = \left[\left(5{,}977{,}100 - 2{,}000{,}900 \right) / \; 2{,}977{,}300 \right] (0.5)(100)$$

$$= 67 \pm 20 \ \%$$

* Same products in both flowsheets except for nickel (nickel in modified flowsheet) and chromium (chromium oxide in modified flowsheet).

See Section 8.15 for details.

computer technology. Process modeling, microprocessor control and robotics technology will play key and cost effective roles in process optimization. Falling prices for all computer technology will enable even the smallest company to benefit from these techniques. The main obstacle to this computerization and optimization will be the availability of software specific to the needs of the metallurgical industry.

Process modeling (especially mass and energy balance modeling) has long been recognized as an engineering technique that enables metallurgical staff members to design and operate efficient systems. However, these techniques involve many tedious, repetitive and time consuming calculations, and are, thus, very labor intensive. Operating plants, particularly small operations, often cannot afford to involve engineers in such modeling even if plant materials and energy are wasted in the process. Process modeling and/or optimization could be a viable technique for any operation if the lengthy, repetitive calculations were coded into computer programs. Low cost, powerful personal computers can make such process modeling an effective tool for each engineer.

Mathematical process modeling of any metallurgical unit operation can provide plant operators with an incalculable amount of information concerning plant practices. Mass balances can track the path of one or twenty or fifty items (such as metal ion concentrations) throughout the entire series of unit operations. Recycle streams, changing flow velocities and mass additions can turn simple mathematical calculations into a repetitious, time gobbling nightmare. Keeping track of even one concentration or volume throughout the entire series of unit operations can be extremely time consuming at best. Changing one variable changes all calculations and starts the repetitious process again. Tracking several important values can be an itemized accounting mess. Process modeling of several interacting unit operations can exponentially increase time consumption. It is simply too time consuming to play "what if" with the process model if the calculations are done by hand.

Fortunately, the mathematical calculations involved in these mass and energy balances are simply matters of repititious additions, subtractions, multiplications and divisions. The process variables and the items to be tracked can be often divided into a series of arrays. These conditions are simply perfect for computer coding. Once the process calculation scheme is developed, even a personal computer can trace several values at once. Disk storage techniques can be employed to track an almost limitless (within reason) amount of interacting items.

The research completed in this study investigated the use of an 8-bit personal computer, an Apple II+, to model the mass balance calculations for the extraction of metal values from mixed metal hydroxide electroplating sludges. The models are, at this point in time, computerized mass balances that model various extractive metallurgical unit operations. These models can be easily adapted for optimization studies at a later date.

Several metallurgical unit operations were utilized in the extraction of the various metal values contained in the electroplating sludges. Therefore, several models were necessary to describe the research system. Also, these models must "interact" so that the entire system could be researched. In other words, the outflow of one unit operation model would be the inflow of the next unit operation model. The models were, thus, designed with this inflow/outflow concept. However, as will be demonstrated later, this inflow/outflow concept is an option to the computer operator. The operator can choose to have the outflow of the last unit operation be the inflow of any of the listed unit operations or provide a new inflow. This allows the user complete flexibility within the complete series of unit operation models and makes "what if" designing very easy.

This research completed the following computer assisted mass balance models. It should be noted that these models were designed to describe a specific extraction system and were not intended to be general models for any system. However, modifications can be made to these programs fairly easily, and, they could be changed to define other systems as well. These models are:

- Composite Sludge

  This program allows the user to mix as many as 12 sludges together to provide a composite sludge that will serve as the input sludge to the leaching operation.

- Recycle Solids

  This program allows the user to add recycle solids to the leach vessel.

- Leach

  This program models the leaching of the combined electroplating sludges with sulfuric acid and water. Three recycle streams may be added to the vessel.

- Solid/Liquid Separation

  This program models solid/liquid separations that involve filtering and additions of wash water. Three different washing operations are permitted.

- Solvent Extraction

  This program models solvent extraction unit operations with a maximum of three stages. The operator also has the option of stripping the loaded organic.

- Precipitation

  This is a general extraction model that allows the operator to remove metal values from solution. The operator may choose precipitation of a species or may remove metal values with a "black box" method so that the resulting stream may be the input to the next operation. This is an especially useful method for "what if" calculations.

All of the models monitor important parameters with respect to 12 metals - Cu, Ni, Cd, Zn, Cr, Ca, Na, Fe, Al, Pb, Si and P.

6.5.2. Instructions

The diskettes and the instructions are provided as a separate document. Example output of the calculational program is presented in Table 8.147 for the 50 ton per day cost analysis flowsheet.

SECTION 7

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SECTION 8

APPENDICES

8.1. ANALYTICAL PROCEDURES

8.1.1. Sludge Dissolution and Analyses

The dissolution of the sludge material was performed by the following procedure:

- A 100 pound sample was removed from the barrel of sludge. The sludge was chopped up with a laboratory mixer into pea size particles.
- The sample was blended by repeated mixing.
- One hundred gram samples were split from the blended material and placed in a drying oven at 100°C for 24 hours. Samples were weighed and moisture content calculated. Samples were run in quadruplicate to verify results.
- The dried material was ground in a mortar and pestle to -100 mesh. A 5.00 gram sample was split from the ground material.
- The dried and sized sample was digested to determine composition.
- A 5.00 gm sample was carefully weighed and placed in a 400 cc beaker. 100 cc of aqua regia was added to the beaker plus 25 cc of perchloric acid.
- The slurry was placed on a hot-plate and fumed to a semi-dry state. The sample was cooled and redissolved in 100 cc of 10% HCl solution.
- The solution was transferred to a 500 ml volumetric flask and diluted to volume. A reagent blank was carried along through the entire procedure for matrix correction.
- The digested sample solution was analyzed for element content by ICP spectrophotometry.

8.1.2. Aqueous Phase Analyses

Aqueous phase analyses were performed by ICP procedures. A solution sample was withdrawn from a test sequence, filtered (if necessary), placed in a 25 cc polyethylene vial and capped. The sample was assigned an analytical number in a master record book. Each sample number was recorded and a brief one line description written beside it. Dilution, if any, of the solution was recorded in the test notebook. The sample was then supplied to the project's chemist. Most samples were analyzed within three days by ICP spectrophotometric analysis. All dilutions performed by the chemist are reported in the analytical computer print-out for each individual sample. All results from the analytical laboratory were reported in mg/l.

An EPA performance evaluation set of aqueous samples was supplied to Montana Tech Foundation for determination of solution metal contents. The results are presented in Table 8.1.

The results of the performance evaluation showed that all elements were rated acceptable except for the element iron. The cadmium rating was "check" which means the results were within the acceptable range but outside the "warning range".

Iron was run using a defective AA lamp and the problem was rectified with a new lamp.

A majority of the Phase I aqueous samples were run on an Yvon ICP model JY 48 spectrophotometer. The Phase II analytical work was performed in a Perkin-Elmer ICP Model 5500. However, initial and subsequent periodic checks were made to assure that the results compared favorably with atomic absorption results.

It was desirable to analyze a number of samples for the Fe^{++}/Fe^{+++} contents. The analytical technique used for Fe^{++} content followed the procedure: The chief interference with the FeII determination is from high Ni concentration which obscure the endpoint. Thus, a small volume of sample is used and diluted to about 50 ml.

TABLE 8.1. PERFORMANCE EVALUATION REPORT: 12/03/82 WATER POLLUTION STUDY NUMBER WP 009

Parameter	Sample No.*	Montana Tech Foundation Value(mg/l)	True Value (mg/l)	Acceptable Limits (mg/l)	Warning Limits (mg/l)	Performance Evaluation
Aluminum	2	0.94	0.968	0.789 - 1.220	0.844 - 1.170	Acceptable
Cadmium	2	0.06	0.072	0.057 - 0.086	0.061 - 0.082	Check
Chromium	2	0.31	0.270	0.203 - 0.330	0.219 - 0.314	Acceptable
Copper	2	0.33	0.338	0.289 - 0.370	0.300 - 0.368	Acceptable
Iron	2	0.14	0.990	0.839 - 1.110	0.873 - 1.080	Not Acceptable**
Nickel	2	0.38	0.400	0.324 - 0.470	0.342 - 0.450	Acceptable
Zinc	2	0.45	0.420	0.373 - 0.462	0.384 - 0.451	Acceptable

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* Calibration on Perkin Elmer 403 Atomic Absorption Spectrophotometer set up for hundredths of mg/l level; not calibrated for g/l. Therefore, all No.1 samples not valid test of capabilities.

** Iron hollow cathode tube defective.

To a 125 ml Erlenmeyer flask add 50 ml H_2O (deionized), 15 ml 20% H_2SO_4, and 2 mls of H_3PO_4. Pipet in 1.0 ml of sample and add 8 drops of sodium diphonylamine sulfonate indicator. Titrate using moderate quantities of dichromate while stirring or swirling. Proceed slowly with small volumes of dichromate near the endpoint. When a violet color persists for one minute, the endpoint has been reached. It is best to perform triplicate determinations until volumes agree to within ± .02 ml.

Report as gpl using:

$$Fe^{++} \text{ gpl} = \frac{(\text{vol. } 0.001N \text{ dichromate})(55.85)}{1000}$$

The reagents required for Fe^{++} determination include:

- Potassium dichromate solution (0.2 N) made by drying pure $K_2Cr_2O_7$ @ 120°C and dissolving 4.9040 gm in one liter of deionized H_2O. Dilute to 0.001 N solution.
- H_2SO_4 solution; 20 v/o.
- Sodium diphenylamine sulphonate solution: 0.16 w/o.
- Concentrated H_3PO_4.

The ferric iron content of the aqueous phase was determined by subtracting the Fe^{++} content from the total solution iron content.

Chloride and sulfate anion determinations were performed using a DIONEX System 10 Anion Chromatograph. The procedure was: dilute the sample, 1/500, with millipore treated deionized water; then analyze on the DIONEX system. (Standards from 2000 g/ml $SO_4^=$ and Cl^- should be made in such a manner to bracket the concentrations in the sample).

Chromate or dichromate anion concentration was determined by the following procedure:

- Determine the total chromium content of the solution by AA or ICP.
- Expose a known volume of solution to an equal volume of IRA 900 (a strongly basic ion exchange resin). This quantitatively removes the $CrO_4^=$, $Cr_2O_7^=$, or $HCrO_4^-$ anions.

Measure the volume of solution and analyze the recovered solution by AA or ICP.

Wash the resin with water and collect the wash solution, measure the volume and determine the total chromium content of this sample (Cr^{+3}).

Calculate the oxidized chromium in mg.

8.1.3. Organic Phase Analyses

Reagents:

Solvents: Two solvents are currently in use on a routine basis in laboratories using ICAP Spectrometry on organic solutions; these are MIBK (methylisobutyl ketone-spectral grade) and Xylene (mixed or para isomer-spectral grade). The first solvent is highly polar, meaning its wettability of the sample uptake capillary is "well behaved" - similar to water; however, it has a high vapor pressure and tends to produce an intense emission in the plasma. It is also highly corrosive of most tubing materials. Xylenes are non-polar and have a reasonably lower vapor pressure than MIBK. Since they do not wet the nebulizer in an acceptable fashion, the use of a peristaltic pump is highly recommended to insure reproducible sample flow rates.

Standards: Single element standards and a mixed element standard containing 21 elements (S-21) are available from: Conoco, Inc., Ponca City, Oklahoma. The standards carry the brand name conostan and can be purchased in a variety of concentrations. It is highly recommended that single element standards be purchased in order that spectral interferrons can be quantified and standard addition procedures may be employed in sample analyses where necessary.

Procedure:

JY 48 Instrument parameters must be set differently for aqueous and organic solutions. The incident power is increased and the sample flow rate is reduced considerably (an order of magnitude for MIBK). Also, auxiliary plasma gas is used to raise the bottom of the plasma one-half the distance from the

Teflon support block (approximately equal with the top of the torch tip) to the first load coil. This prevents carbon buildup in the torch.

Instrument Parameters:

	Incident RF	Fine Tune	Neb* Pressure	Neb* Flow Rate	Sample Uptake
MIBK	1.5 Kw / 4-5w Ref.	7.1	20 psi	.52	0.20 ml/min.
Xylenes	1.75 Kw / 4-5w Ref.	3.5	28 psi	.50	1.98 ml/min.

*Nebulizer: Meinhart T230B2 concentric glass.

With typical solvent extraction type organic samples from metallurgical process streams, the necessary dilution factor is 1/1000. This obviates any special considerations one might have to give the sample because of unique physical properties such as high viscosity, since the diluted sample is mainly solvent.

Once the instrument parameters are optimized and inter-element corrections quantified, analysis is as routine as aqueous samples.

8.2. SULFURIC ACID LEACH STUDIES

8.2.1. Preliminary Testwork

Sulfuric acid is a very effective lixivant for treating mixed metal sludge material. The design matrix and experimental results are presented in Table 8.2. All experimental tests were run in a thermostated one liter leach vessel under specified conditions of time, temperature, sulfuric acid concentration, Eh, air purge, and agitation rate. One to two hundred gram samples of undried sludge were leached with 250 cc of leach solution. Solution samples were analyzed by Induction Coupled Plasma Spectrophotometry (ICP).

TABLE 8.2. DESIGN MATRIX FOR SULFURIC ACID LEACHING OF SLUDGE (1/8 REPLICA): SERIES ONE

Results: Extraction from Solid (%)

Sample		Time (Hrs.)	Temp. (°C)	H_2SO_4 (gpl)	Eh (% HNO_3)	Air Purge	Agitation Rate (RPM)		Cu	Fe	Cr	Ni	Zn	Cd
	Base	1.0	20°	90	5	No	370							
	Unit	0.5	---	20	5	--	--							
	High (+)	1.5	80°	110	10	Yes	560							
	Low (-)	0.5	20°	70	0	No	210							
	Test No.								Cu	Fe	Cr	Ni	Zn	Cd
338 & 246	1	-	-	-	-	-	-		84.1(89.9)	85.5 (93.7)	(91.2)(100.0)	86.1(90.3)	97.2(103.3)	100(100)
339	2	+	+	-	-	+	+		92.8	97.5	100	97.9	100	100
291	3	+	-	+	-	+	-		98.6	100	100	99.3	100	100
314	4	-	+	+	-	-	+		89.9	98.1	100	91.7	100	100
315 & 292	5	+	-	-	+	-	+		89.9(88.4)	96.5 (96.5)	(100)(100)	92.4(87.5)	100(98.1)	100(100)
356	6	-	+	-	+	+	-		89.9	95.3	97.0	85.4	100	100
337	7	-	-	+	+	+	+		95.7	100	100	95.1	100	100
312	8	+	+	+	+	-	-		94.2	100	100	84.7	100	100
261-3	Baseline								70.0±4.8	74.6±4.5	81.1±3.6	69.2±5.4	77.7±8.0	83.3±6.7
								Max. Exp. Variation	±6.8	±6.0	±4.4	±6.6	±10.3	±8.0

Effects	Time (Hrs.)	Temp. (°C)	H_2SO_4 (gpl)	Eh (% HNO_3)	Air Purge	Agitation Rate (RPM)
Cu	-0.2	2.7	0.5	2.0	0.2	0.2
Fe	1.1	2.9	1.3	1.9	0.9	1.4
Cr	0.7	1.5	0.7	1.5	0.7	1.5
Ni	-1.6	1.1	-2.2	2.0	0.6	2.7
Zn	0	0	0	0	0	0
Cd	0	0	0	0	0	0

NOTE:

- Sludge 5. Solids Composition (%) 14.52±0.25 Fe, 1.57±0.02 Cr, 3.17±0.03 Cu, 6.62±0.04 Ni, 9.68±0.08 Zn, 0.48±0.02 Cd
- Tests 2 and 5 duplicated
- Baseline Run Three Times
- 70 gpl Sulfuric Acid is Approximately the Stoichiometric Acid Requirement.

The data in Table 8.2. illustrate excellent metal value extraction. The effects portion of the table illustrates that the variation in experimental conditions chosen for study do not significantly influence metal value recovery; e.g., for copper the percent extraction is changed only by: -0.2% per 0.5 hr. increase in leach time; 2.7% per $60^{0}C$ increase in temperature, etc. The design matrix was repeated to consider the influence of acid content and of sludge/liquid ratio. The results are presented in Table 8.3. The variable (for the range studied) that shows the greatest influence on all metal value extractions is acid content. Refer to the effects data in Table 8.3 for the influence of each variable on individual metal extractions.

The design matrix tests resulted in acid solutions that had pH values in the range 0.5-1.5. A series of experiments were performed to investigate the influence of pH on metal extraction. The results are presented in Table 8.4.

Two of the design table leach residues (Test 3 No. 291 and Test 6 No. 356) were photographed and selected sections of the filtered solid were compared by SEM analyses. The results are presented in Figures 8.1, 8.2, and 8.3, Tables 8.5 and 8.6. Note in the photographs that the filtered solids contain a variety of materials, e.g., sand-like particles, wood fibers, etc.

Leach residue samples were prepared for three of the design matrix tests, i.e., samples were leached using the same conditions as specified in the design table for Baseline (No. 261); Test 3 (No. 291); and Test 6 (No. 356) conditions. Comparisons between the energy spectra for starting sludge and leach residues are presented in Figures 8.4, 8.5, and 8.6. A quantitative analysis of the same three residues is presented in Table 8.7.

The influence of time and solid/liquid ratio on metal value extraction is illustrated in Figure 8.7 and in Tables 8.8 and 8.9. Note that the leach conditions for the test are baseline conditions and not optimum conditions. However, the data do illustrate that the dissolution is very rapid.

A complete mass balance on a typical leach system was conducted to assure that analytical results were reliable. The results are presented in Table 8.10.

TABLE 8.3. DESIGN MATRIX FOR SULFURIC ACID LEACHING OF SLUDGE (1/8 REPLICA): SERIES TWO

Sample		Time (min.)	H_2SO_4 (% of Solids)	Sludge/ Liquid Ratio	Agitation (RPM)	Temp. (°C)	Eh (% HNO_3)		Results: Extraction from Solution (%)					
									Cu	Fe	Cr	Ni	Zn	Cd
	Base	30	55	200 gm/ 250 cc	370	25	5							
	Unit	15	25	100 gm/ 250 cc	-	-	5							
	High (+)	45	80	300 gm/ 250 cc	560	50	10							
	Low (-)	15	30	100 gm/ 250 cc	210	25	0							
	Test #													
885	1	-	-	-	-	-	-		36.7	0.6	10.7	11.8	45.8	53.1
886	2	+	-	-	+	-	+		89.8	88.3	85.4	26.2	89.2	86.4
887	3	-	+	-	+	+	-		79.6	66.4	71.2	23.6	81.1	79.7
888	4	+	+	-	-	+	+		90.6	88.6	85.4	26.7	91.7	93.0
889	5	-	-	+	+	+	+		67.9	22.0	39.2	55.2	71.7	81.9
890	6	+	-	+	-	+	-		30.2	0.3	3.6	30.1	49.4	66.4
891	7	-	+	+	-	-	+		94.7	91.1	83.1	80.7	93.5	100.0
892	8	+	+	+	+	-	-		86.1	71.2	71.2	73.4	87.2	95.2
882-4	Base								71.9±1.8	68.6±2.0	67.0±2.4	65.9±2.3	80.6±3.1	83.1±3.3

Effects (%)						
Cu	2.2	15.8	-2.2	8.9	4.9	13.8
Fe	8.5	25.8	-7.4	8.4	-9.2	18.9
Cr	5.1	21.4	-6.9	10.6	-6.4	17.0
Ni	-1.9	10.1	18.9	3.6	-7.1	6.2
Zn	3.2	12.2	-0.8	6.1	-2.7	10.3
Cd	3.3	10.0	3.9	3.8	-1.7	8.4

NOTE:

- Sludge Barrel 2.
- Solid Composition (%): 16.08±0.50 Fe, 5.70±0.14 Cu, 1.25±0.04 Cr, 6.16±0.15 Fe, 10.87±0.31 Zn, 0.67±0.02 Cd
- Sludge solid content: 24.47%
- Sludge/liquid ratio: gm sludge/250cc solution
- (Solid/liquid) wt. ratio = $\dfrac{(\text{gm sludge})\left(\frac{\%\text{solid}}{100}\right)}{\text{gm } H_2O \text{ added} + \text{gm } H_2O \text{ in sludge} + \text{gm } H_2SO_4 + \text{gm } HNO_3}$

TABLE 8.4. INFLUENCE OF PH ON METAL EXTRACTION FROM ELECTROPLATING METAL HYDROXIDE SLUDGES

Sample	Condition	Metal Extraction from Solid (%)					
		Cu	Fe	Cr	Ni	Zn	Cd
533	pH = 0.5	94.7	97.4	99.4	95.9	97.0	93.0
534	1.0	89.9	91.3	94.7	92.9	91.8	93.0
535	1.5	93.7	92.0	96.5	95.9	95.1	93.0
536	2.0	79.5	46.7	71.8	87.4	79.5	84.8
537b	3.0	49.3	0.6	17.0	52.2	55.5	69.7
538	4.0	13.5	<0.03	5.1	20.4	31.8	46.5
539	5.0	1.7	<0.03	5.1	12.7	14.1	23.3
540	6.0	0.5	<0.03	5.4	9.4	2.2	<0.03

NOTE: ·Sludge Barrel 1
Composition (%): 18.27±0.44 Fe, 7.84±0.40 Cu, 1.17±0.06 Cr, 5.53±0.33 Ni, 11.47±0.47 Zn, 0.73±0.04 Cd
·Solid content of sludge: 23.56%
·100 gm sludge $\left(\begin{array}{l}23.56\text{ gm solids}\\76.44\text{ gm } H_2O\end{array}\right)$ slurried in 200 cc H_2O + X grams H_2SO_4
·Time: 30 minutes
·Temperature: 25°C

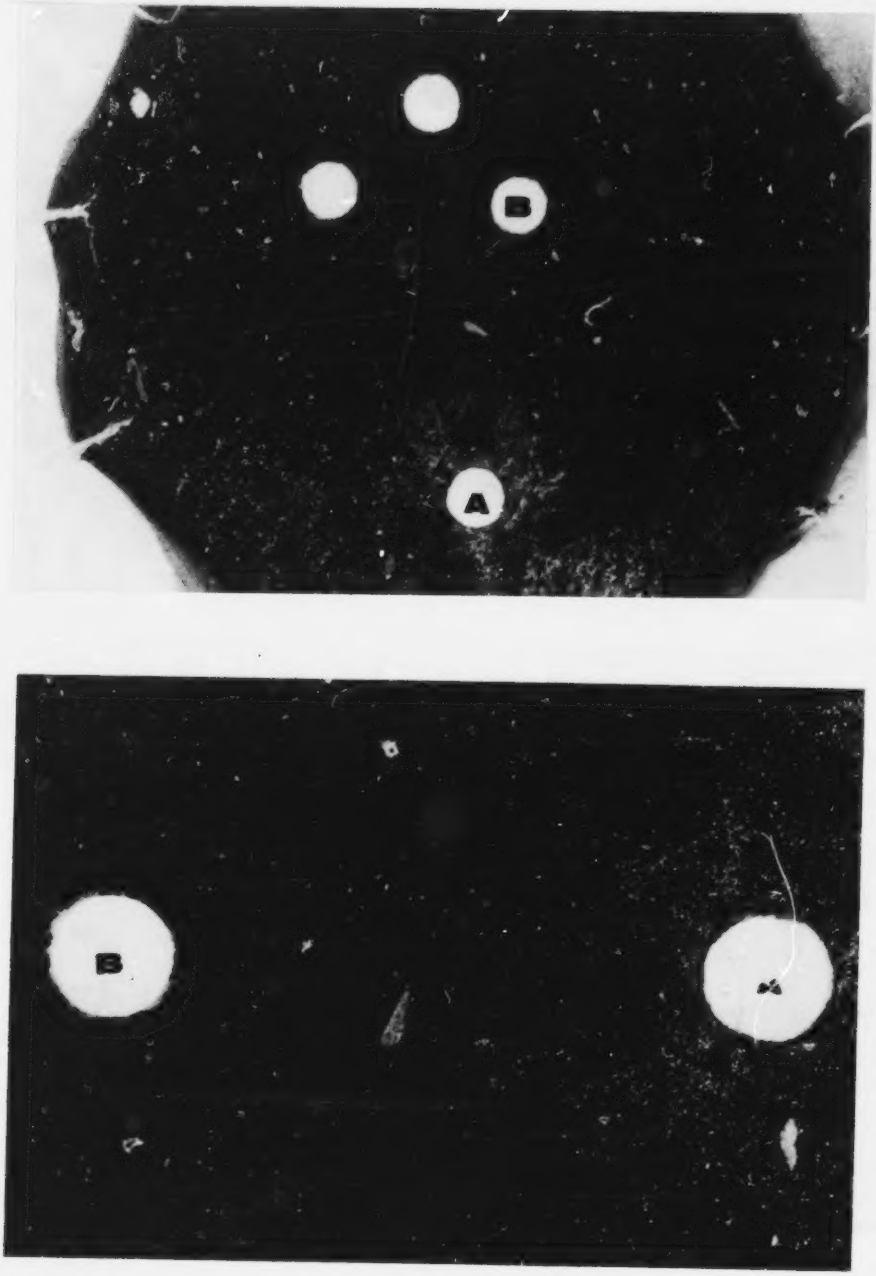


Figure 8.1 Photograph of residue from design matrix test no. 6.

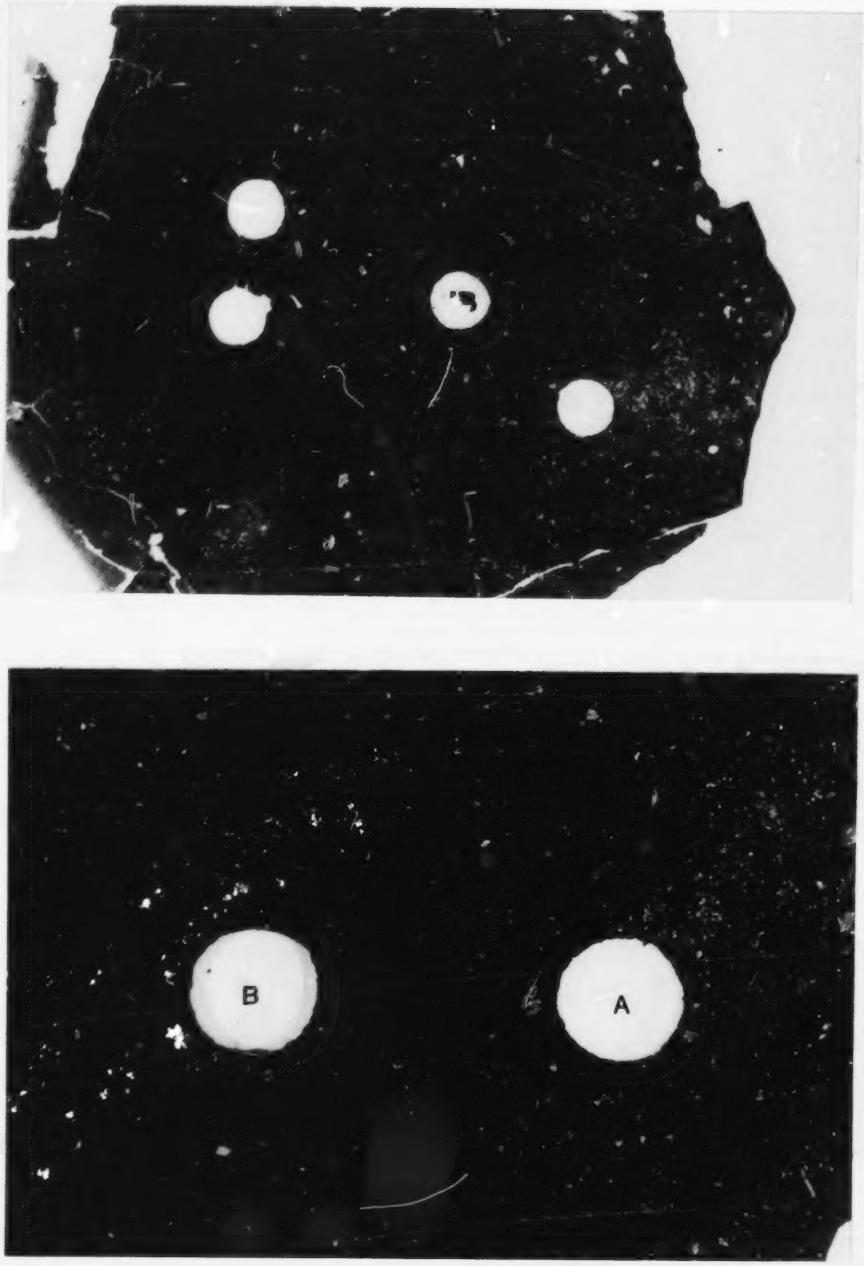
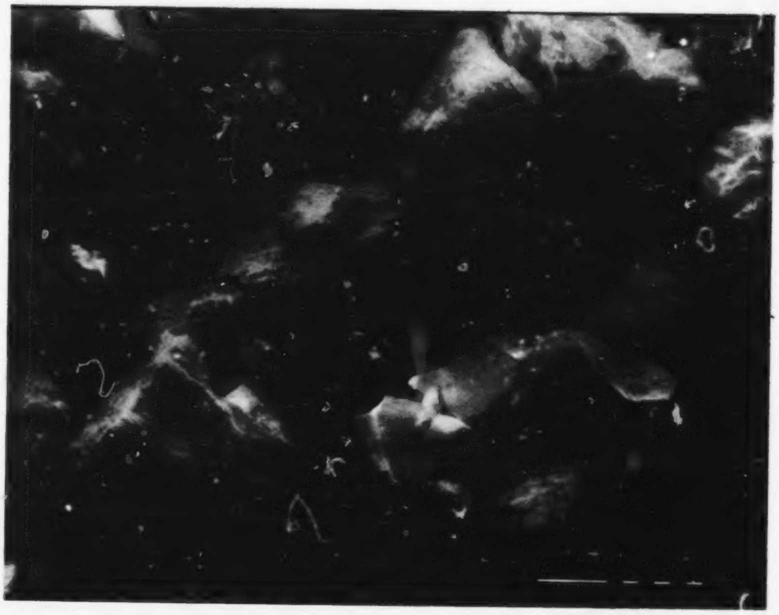


Figure 8.2. Photograph of residue from design matrix test no. 3.



100X

Figure 8.3. SEM photomicrograph of section A from design matrix no. 6.

Reproduced from best available copy.

TABLE 8.5. SEM THIN SECTION ANALYSIS OF DESIGN MATRIX TEST THREE RESIDUE (TEST SAMPLE 291)

	Composition (%)	
Element	Section B	Section A
Cu	3.59	2.78
Fe	8.88	7.14
Cr	0.46	0.29
Ni	0.53	0.21
Zn	1.46	0.69
Cd	0	0
Si	18.56	27.14
Al	2.10	6.30
Ca	0.26	1.11
S	12.28	3.55
P	0.17	0
Cl	1.09	0.06

A: Leach residue 291 sample taken from the area marked A in Figure 8.2.

B: Leach residue 291 sample taken from the area marked B in Figure 8.2.

TABLE 8.6. SEM THIN SECTION ANALYSIS OF DESIGN MATRIX SIX RESIDUE (TEST SAMPLE 356)

	Composition (%)	
Element	Section B	Section A
Cu	3.88	2.18
Fe	9.39	7.79
Cr	0.64	0.29
Ni	2.04	0.72
Zn	0.94	0.35
Cd	0	0
Si	21.69	26.56
Al	3.76	8.25
Cr	0.33	1.06
S	5.49	2.09
P	0.29	0
Cl	1.07	0.09

A: Leach residue #356 sample taken from the area marked in Figure 8.1.

B: Leach residue #356 sample taken from the area marked in Figure 8.1.

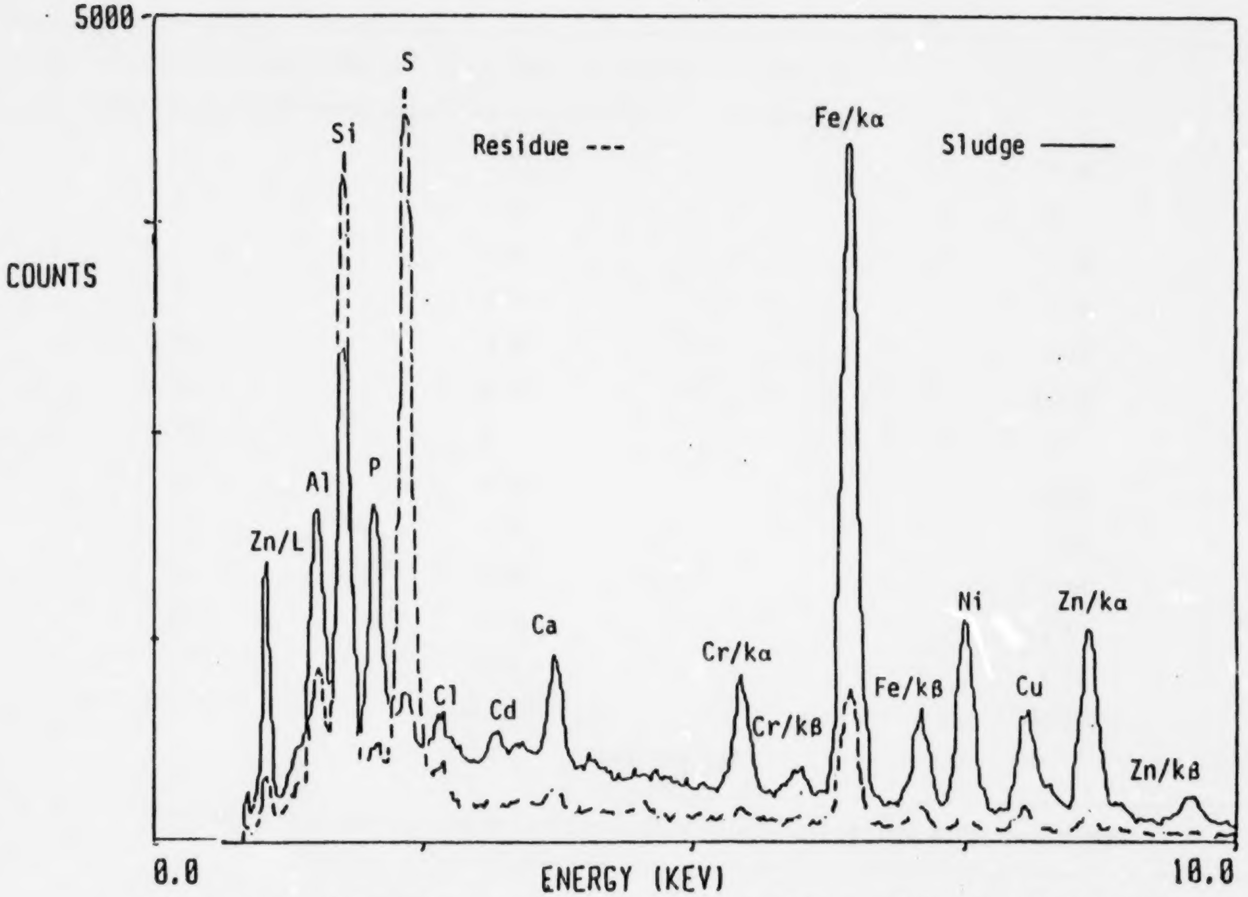


Figure 8.4. Comparsion of unleached barrel 5 sludge and leached sludge residue: Conditions (sample 356) given in table 8.2.

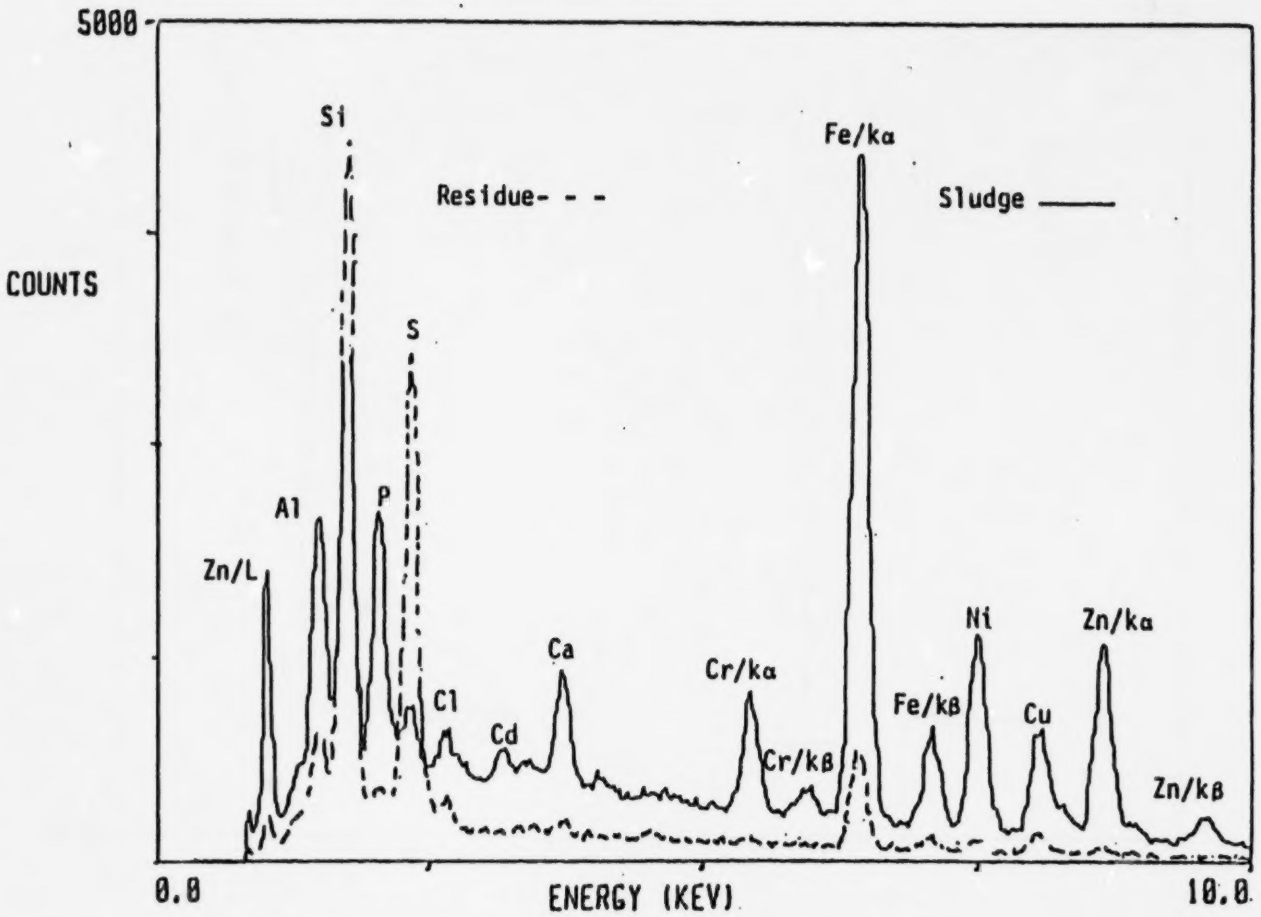


Figure 8.5. Comparsion of unleached barrel 5 sludge and leached sludge residue: Conditions (sample 291) given in table 8.2.

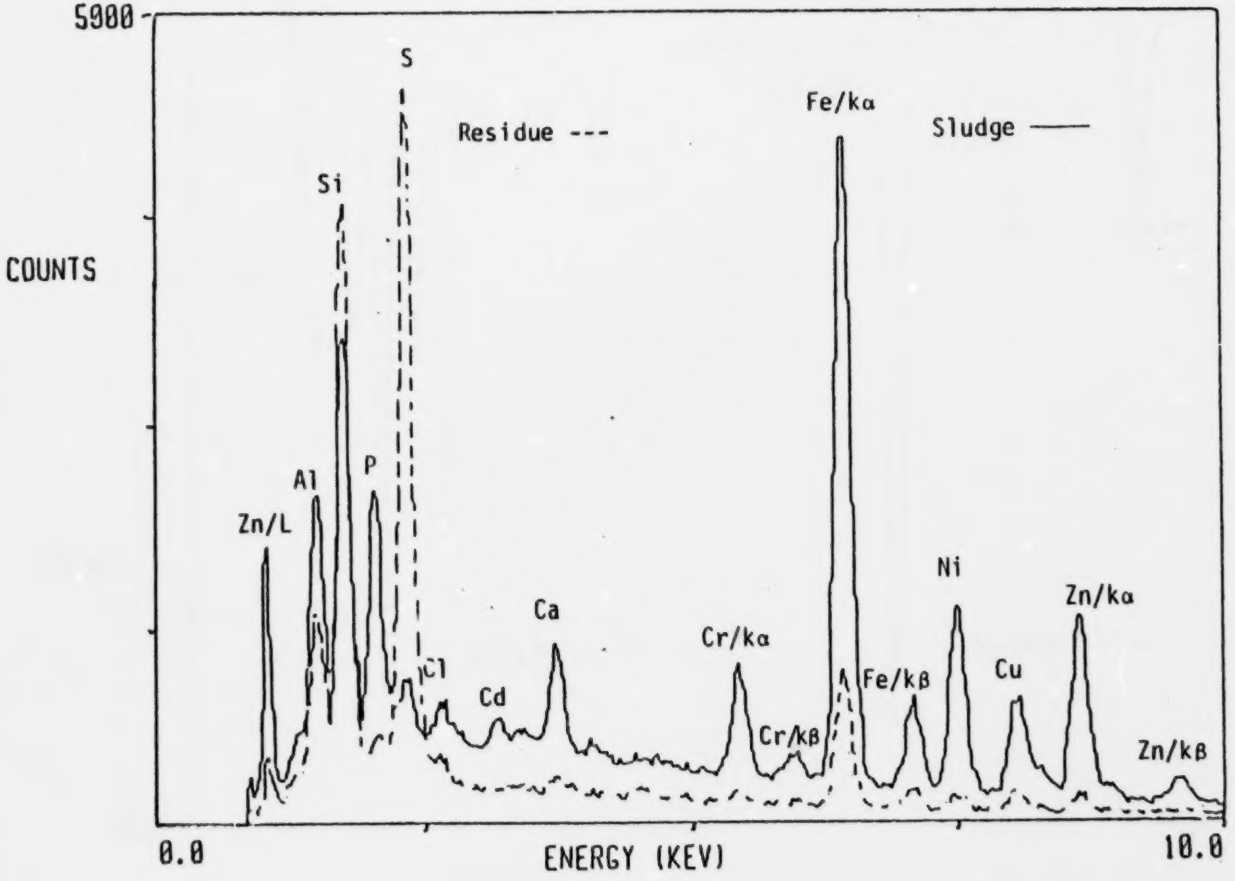


Figure 8.6. Comparsion of unleached barrel 5 sludge and leached sludge residue: Conditions (sample 261) given in table 8.2.

TABLE 8.7. SLUDGE SOLID AND LEACH RESIDUE COMPOSITIONS

Design Matrix Test*	Initial Weight of Solids in Sludge (gm)	Final Weight of Residue (gm)	Composition of Sludge Solids											Composition of Residue Solids										
			Cu	Fe	Cr	Ni	Zn	Cd	Si	Al	Ca	S	P	Cu	Fe	Cr	Ni	Zn	Cd	Si	Al	Ca	S	P
Baseline A (Test #370)	43.44	7.97	4.88	10.23	1.19	3.88	5.92	0.34	7.11	4.29	1.11	0.56	1.30	1.36	2.55	0.35	0.55	0.84	0.16	7.78	2.26	0.38	2.62	0.37
Condition 3 (Test #371)	43.44	7.93	4.88	10.23	1.19	3.88	5.92	0.34	7.11	4.29	1.11	0.56	1.30	1.30	2.48	0.33	0.44	0.70	0.16	8.33	1.79	0.40	2.66	0.40
Condition 6 (Test #372)	43.44	8.81	4.88	10.23	1.19	3.88	5.92	0.34	7.11	4.29	1.11	0.56	1.30	1.45	2.16	0.30	0.51	0.45	0.16	10.13	1.62	0.37	2.10	0.37

* See table 8.2 for leach conditions. Residue 370 resulted from matrix test #261; residue 371 resulted from matrix #291; residue 372 resulted from matrix test #356.

TABLE 8.8. SLUDGE LEACH TEST AS A FUNCTION OF TIME: BASELINE CONDITIONS TABLE 8.2 (8.6% SOLIDS)

Sample No.	Time (min.)	Extraction (%)					
		Cu	Fe	Cr	Ni	Zn	Cd
357-1	5	71.0	65.5	69.4	64.4	71.2	80.1
357-2	15	75.2	71.9	74.1	67.8	76.7	85.7
357-3	30	79.4	76.2	78.6	71.6	81.6	90.8
357-4	45	77.6	75.7	77.9	71.1	80.7	90.1
358 (Repeat of 357)	45	79.6	76.9	79.6	72.3	81.9	92.6
358-1	5	77.2	73.4	77.1	70.9	78.7	89.3
358-2	15	78.3	75.9	79.0	72.4	80.7	91.3
358-3	30	77.1	75.1	78.4	71.6	79.5	90.2
358-4	45	75.9	74.3	77.3	70.5	78.7	88.4
358-5	60	78.8	77.1	79.7	72.3	81.6	91.1
Comparison to Design Matrix Baseline Conditions (Table 8.2)		70.0 ± 4.8	74.6 ± 4.5	81.1 ± 3.6	69.2 ± 5.4	77.7 ± 8.0	83.3 ± 6.7

Notes: . 20°C, 90 gpl H_2SO_4
. 100 g sludge barrel 5/250 cc solution, 21.75% solids in sludge.

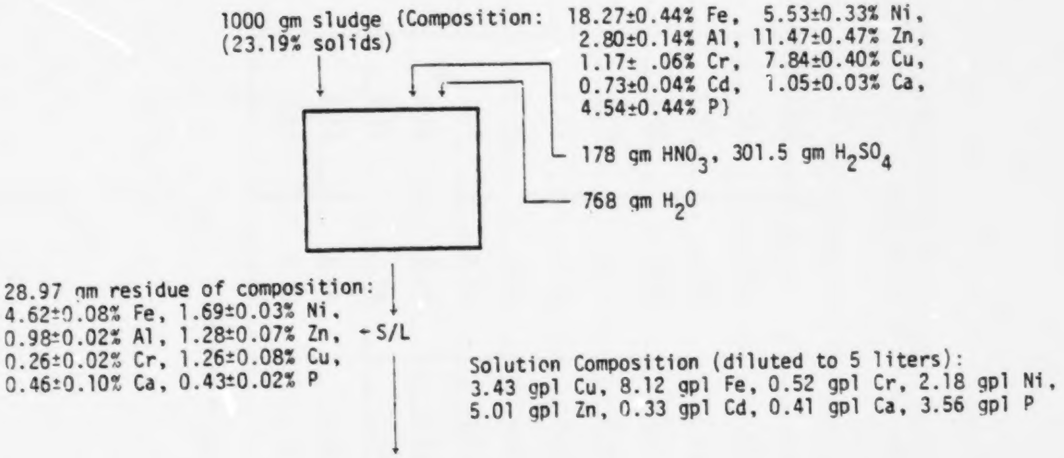
TABLE 8.9. SLUDGE LEACH TEST AS A FUNCTION OF TIME: BASELINE CONDITIONS IN TABLE 8.2 (16.2% SOLIDS)

Sample No.	Time (min.)	Extraction (%)					
		Cu	Fe	Cr	Ni	Zn	Cd
252-1	10	54.3	42.1	73.3	60.6	50.3	82.5
2	30	63.4	62.0	85.6	61.7	45.8	82.5
3	50	54.3	57.2	65.2	57.3	45.8	82.5
4	90	65.6	49.7	73.3	66.3	45.8	96.2
5	120	61.1	62.0	48.9	58.4	48.3	82.5
6	150	61.1	45.4	57.1	71.6	48.3	82.5
7	180	63.4	59.2	69.3	66.1	45.8	82.5
8	210	61.1	47.3	77.4	65.1	52.8	96.2
9	240	61.1	47.3	73.3	71.7	51.0	96.2
10	270	61.1	42.4	77.4	58.4	45.8	82.5

Notes: . 20oC, 90 gpl H_2SO_4
. 200 g sludge, 22.72 % solids in sludge

TABLE 8.10. MASS BALANCE ON LEACH #532

Conditions of leach:
- 1000 gm sludge in 1250 cc of leach solution (Barrel 2).
- Time : 30 min.
- Temp. : 43-53°C
- H_2SO_4 : 130% of solids, i.e., 163cc H_2SO_4
- 10% HNO_3
- Agitation:



1000 gm sludge (Composition: 18.27±0.44% Fe, 5.53±0.33% Ni, 2.80±0.14% Al, 11.47±0.47% Zn, 1.17± .06% Cr, 7.84±0.40% Cu, 0.73±0.04% Cd, 1.05±0.03% Ca, 4.54±0.44% P)
(23.19% solids)

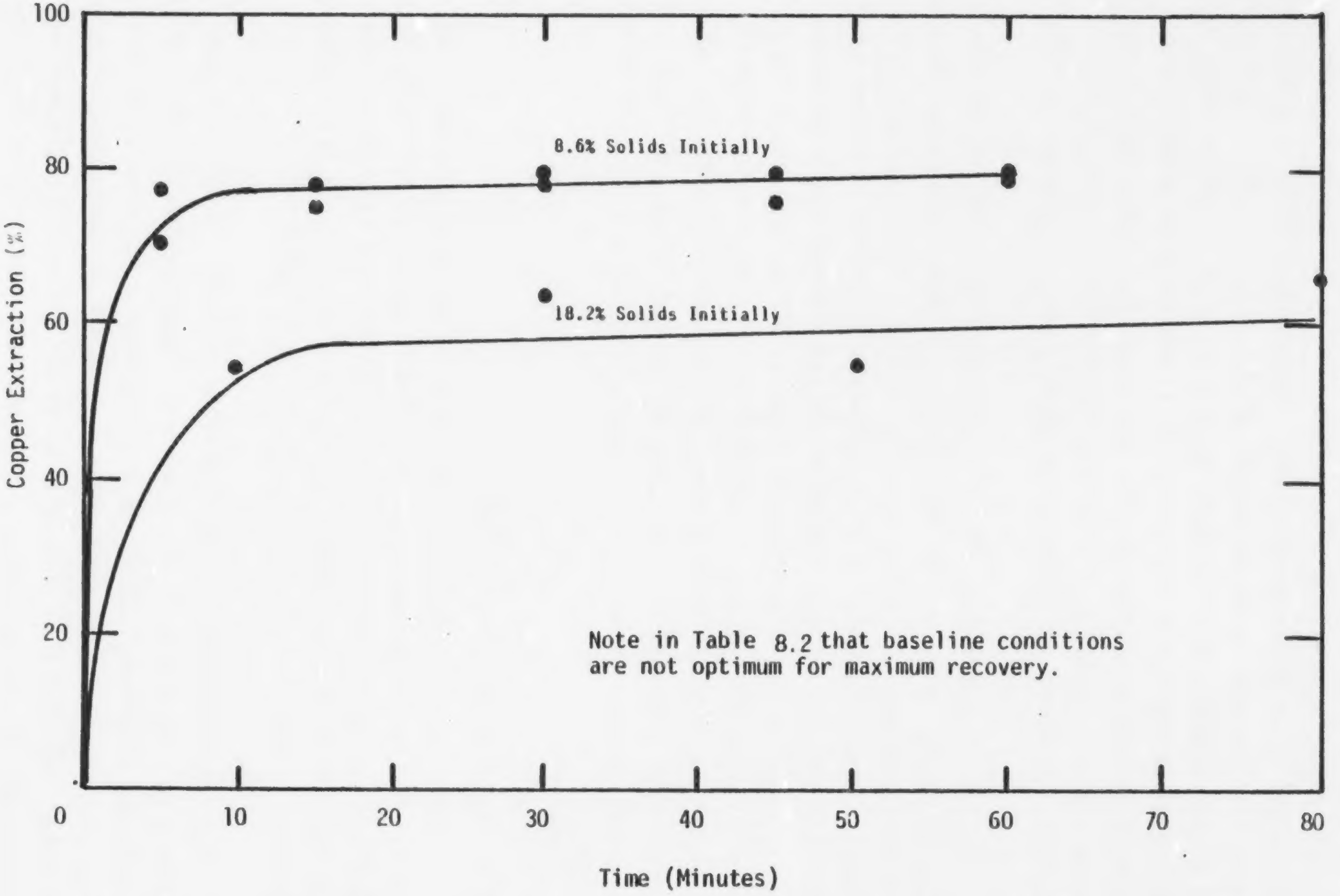
178 gm HNO_3, 301.5 gm H_2SO_4

768 gm H_2O

28.97 gm residue of composition:
4.62±0.08% Fe, 1.69±0.03% Ni,
0.98±0.02% Al, 1.28±0.07% Zn,
0.26±0.02% Cr, 1.26±0.08% Cu,
0.46±0.10% Ca, 0.43±0.02% P

Solution Composition (diluted to 5 liters):
3.43 gpl Cu, 8.12 gpl Fe, 0.52 gpl Cr, 2.18 gpl Ni,
5.01 gpl Zn, 0.33 gpl Cd, 0.41 gpl Ca, 3.56 gpl P

	Element Weight Balance (Grams)						
Material	Cu	Fe	Cr	Ni	Zn	Cd	Al
Starting Solid	18.18	42.37	2.71	12.82	26.60	1.69	6.49
Leach Solution	17.15	40.60	2.62	10.90	25.05	1.64	6.50
Leach Residue	0.37	1.34	0.08	0.57	0.37	0	0.28
Unaccounted (%)	-3.6	-1.0	-0.4	-10.5	-4.4	-3.0	+4.5



Note in Table 8.2 that baseline conditions are not optimum for maximum recovery.

Figure 8.7. Influence of initial solid content on copper extraction from sludge as a function of leach time: Baseline conditions table 8.2.

Conditions for a standard leach test were chosen and all subsequent testwork was based on these conditions: Temperature, 45-50°C, produced by in-situ reaction heat and acid heat of dilution; time, 0.5 hr.; acid content, 100% of solid weight (this produces an acid solution in the pH range 0.5-1.5); moderate agitation to suspend all solids in the solution phase; and a sludge/liquid ratio of 0.8. A large number of leach tests, both in kettle reactor and on a larger scale, confirm that sulfuric acid extractions are excellent. A summary of a portion of these tests is presented in Table 8.11.

The leach procedure was found to produce pebble-like agglomerates of unleached sludge if the sludge was slurried in water followed by addition of acid then agitated. Extensive agitation failed to break up these agglomerates. However, if the sludge was first exposed to concentrated acid then water added to produce the desired acid concentration, agglomeration did not occur. The leach procedure adopted consisted of blending the solids; adding the solids to the reaction kettle; adding concentrated sulfuric acid (this raised the system temperature to about 50-60°C) to the sludge; initiating agitation; adding dilution water; then allowing reaction to proceed for one-half hour. All of the sludge materials tested in this study responded well to sulfuric acid leaching.

8.2.2. Large Scale Leach Testwork

Leach of 75-100 pounds of sludge in a single batch unit operation appears to offer no chemical or mechanical problems. The extraction is rapid and controllable. Excellent extractions are achieved for all metal values of interest. Detailed experimental data for five large scale leach tests are presented in Section 8.13. and are summarized in Table 8.11.

The test procedure is described in Section 5.1. Briefly it consisted of blending a large sample of sludge material; sampling for moisture and chemical composition determination; adding the sludge to a 120 liter or 270 liter vessel; adding concentrated sulfuric acid slowly to the sludge; diluting with tap water; and initiating agitation by an air driven one-horsepower agitator. Reaction was considered complete after one-half hour. All of the large scale

TABLE 8.11. EXAMPLES OF METAL VALUE RECOVERY BY SULFURIC ACID DISSOLUTION

Sample No.	Condition	Metal Extracted (%)						
		Fe	Cu	Zn	Ni	Cr	Cd	Al
533	100 g, pH=0.5	96.4	94.7	96.9	95.9	99.4	93.0	89.9
534	100 g, pH=1.0	91.3	89.9	91.8	92.9	94.7	93.0	85.7
535	100 g, pH=1.5	92.0	93.7	95.9	95.9	96.5	93.0	87.1
942	650 g, pH=1.5	95.4	94.9	90.5	97.8	96.7	100.0	95.7
532	1,000 g, pH=1.5	95.8	94.3	94.2	85.0	96.7	97.0	96.0
2116	15,900 g, pH=1.9	62.3	75.9	83.8	82.4	84.6	90.0	90.3
2621	22,700 g, pH=1.5	65.0	92.0	96.9	92.1	92.3	100.0	98.6
2492	50,600 g, pH=1.5	92.0	93.7	95.1	95.9	96.5	93.0	96.9

Note: . All sludge samples were undried.
. H_2SO_4 added equivalent to 100% of solid weight
. One-half hour, 40-50^{o}C
. Sludge/solution = 0.8

leach tests were continued by changing the system conditions to precipitate jarosite into the leach residue.

The results of the large scale test show that metal value extractions achieved were very good and that a significant decrease in solids results, i.e., approximately an eighty-five percent decrease.

8.3. IRON REMOVAL (HIGH IRON BEARING SLUDGES)

Two major studies were conducted to investigate iron removal from leach solutions containing high concentrations of iron (10-20 gpl) and low concentrations of iron (<5 gpl); jarosite precipitation (8.3.1) and solvent extraction of iron (8.3.2). The jarosite precipitation removal of iron is conducted as the first unit operation after leaching and may, in fact, be best performed concurrent with the leach process. The solvent extraction of iron must be conducted after leaching, solid/liquid separation of the leach residue, and solvent extraction of copper.

8.3.1. Iron Removal by Jarosite Precipitation

A commercial technique used for rejection of iron from a metal bearing solution is the jarosite process (1,6,7). There are many forms of jarosite but commercially either ammonium jarosite, $NH_4Fe_3(SO_4)_2(OH)_6$; sodium jarosite $NaFe_3(SO_4)_2(OH)_6$; or potassium jarosite, $KFe_3(SO_4)_2(OH)_6$, are produced. The advantages of the jarosite precipitation process are:

1. Ferric iron can be removed from an acidic solution (pH = 1.5-2.5).
2. The product is a readily filterable form.
3. The precipitation is selective toward iron.

Jarosites are a group of compounds having the general formula:

$$A_x(H_3O)_{(1-X)}Fe_3(SO_4)_2(OH)_6$$

where "A" can be Na^+, K^+, NH_4^+, or H_3O^+. The compounds are naturally occurring and are very stable; they are often referred to as basic iron sulfates. The sodium or potassium ion is preferred in this project because of their relatively low cost. The compounds most likely to precipitate from a sodium containing solution are sideronatrite ($Na_2Fe(SO_4)_2(OH) \cdot 3H_2O$), metasideronatrite ($Na_4Fe_2(SO_4)_4(OH)_2 \cdot 3H_2O$), and natrojarosite ($NaFe_3(SO_4)_2(OH)_6$). The latter is preferred because of its good filtering properties. The compound most likely to precipitate from a potassium containing solution is the posassium analog to natrojarosite, i.e., $KFe_3(SO_4)_2(OH)_6$.

The removal of iron by the jarosite process requires that the iron be present in the ferric form; that the temperature of the solution be as hot as possible (>90^0C); that the pH be maintained within the range 1.5-2.5; and that residence times of several hours be allowed for good crystal growth (to ensure good filtering properties).

8.3.1.1. Small Scale Kettle Testwork

A design matrix for sodium jarosite precipitation and the experimental results are presented in Tables 8.12. and 8.13. As expected the important variables are solution temperature, starting pH, and residence time. The iron in the leach solution is primarily ferric ions so the influence of hydrogen peroxide is minimal. Note also (Table 8.12), that iron is the only element appreciably influenced by the changing variables.

A considerable number of jarosite tests have been performed. Illustrative examples are presented in Tables 8.12. to 8.25. In general two approaches have been taken: (a) the sludge was leached under standard conditions, filtered and a jarosite precipitation study performed on the solutions or (b) the sludge was leached under standard conditions, and a jarosite precipitation study was then initiated "in-situ" leaving the leach residue solids in the reactor. The advantage of approach (b) is that a product is produced that is easily and readily filterable; approach (a) requires that the leach solid be removed prior to the jarosite precipitation. However, the leach residue is very difficult to effectively filter.

The precipitation of iron as a sodium jarosite from a leach solution, Table 8.14., can be compared to precipitation in the presence of the leach

TABLE 8.12. DESIGN MATRIX FOR JAROSITE PRECIPITATION: EXPERIMENTAL DATA (1/4 REPLICA)

Sample		Temp. (^{o}C)	Time (Hrs.)	Na_2SO_4 (stoich.)	Starting pH	H_2O_2	Concentration in Solution (gpl)						
	Base	90	2	2X	2.0	10 cc							
	Unit	---	1	1X	0.5	10							
	High (+)	Boiling	3	3X	2.5	20							
	Low (-)	80^{o}	1	1X	1.5	0							
	Test #						Fe	Cu	Cr*	Ni	Zn	Cd*	Al
943	1	-	-	-	-	-	8.95	2.88	1.28	2.05	5.70	3.35	2.00
944	2	+	-	-	+	-	5.18	2.98	1.13	2.38	5.65	3.13	1.75
945	3	-	+	-	+	+	6.20	3.03	1.20	2.48	5.83	3.28	2.18
946	4	+	+	-	-	+	4.83	2.88	1.08	2.58	5.80	3.35	1.93
947-53	5	-	-	+	+	+	7.68(8.53)	2.93(325)	1.25	2.55(2.55)	5.73(6.00)	3.33(3.38)	2.00(2.28)
948	6	+	-	+	-	+	7.15	2.08	1.25	2.60	6.03	3.43	2.10
949	7	-	+	+	-	-	9.15	3.13	1.30	2.48	5.88	3.28	2.23
950	8	+	+	+	+	-	2.35	2.90	1.05	2.53	5.88	3.33	1.85
951-2	Base						7.50(7.55)	3.18(3.20)	1.30(1.28)	2.48(2.45)	5.85(5.88)	3.23(3.20)	2.20(2.25)
Effect (gpl)													
Fe		-1.6	-0.8	0.2	-1.1	0.0							

*The leach solution was doped with Cr and Cd so that their levels were significant and an evaluation of possible co-precipitates could be determined.

NOTE:
- ·Starting solution composition (gpl) 3.21 Cu, 9.09 Fe, 1.27 Cr, 2.50 Ni, 5.99 Zn, 3.34 Cd, 2.09 Al
- ·200cc of starting solution, volume maintained at 200cc by adding solution adjusted to desired pH
- ·Solids washed on filter with 200cc 5% H_2SO_4 then diluted to 500cc (data corrected to original leach volume)
- ·2 gm jarosite seed added

TABLE 8.13. DESIGN MATRIX FOR JAROSITE PRECIPITATION: EXTRACTION FROM SOLUTION (1/4 REPLICA)

Sample		Temp. (°C)	Time (Hrs.)	Na_2SO_4 (stoich.)	Starting pH	H_2O_2	Extraction from Solution (%)
	Base	90	2	2X	2.0	10cc	
	Unit	-	1	1X	0.5	10	
	High (+)	Boiling	3	3X	2.5	20	
	Low (-)	80°	1	1X	1.5	0	
	Test #						Fe
943	1	-	-	-	-	-	2.0
944	2	+	-	-	+	-	43.0
945	3	-	+	-	+	+	32.0
946	4	+	+	-	-	+	47.0
947-53	5	-	-	+	+	+	16.0(6.0)
948	6	+	-	+	-	+	21.0
949	7	-	+	+	-	-	0
950	8	+	+	+	+	-	74.0
951-2	Base						17.0(17.0)
Effect (%)							
Fe		17.4	8.9	-1.1	11.9	-0.4	

NOTE:
- Starting solution composition (gpl) 3.21 Cu, 9.09 Fe, 1.27 Cr, 2.50 Ni, 5.99 Zn, 3.34 Cd, 2.09 Al
- 200cc of starting solution, volume maintained at 200cc by adding solution adjusted to desired pH
- Solids washed on filter with 200cc 5% H_2SO_4 then diluted to 500cc (data corrected to original leach volume)
- 2 gm jarosite seed added

TABLE 8.14. REMOVAL OF IRON FROM SLUDGE LEACH SOLUTION BY SODIUM JAROSITE PRECIPITATION

Sample	Reaction Time (Hrs.)	Solution pH	Concentration in Solution (gpl)						
			Fe	Cu	Zn	Ni	Cr	Al	Cd
896	0	2.1	8.61	3.80	5.77	2.69	0.58	1.39	0.39
897	1	2.0	3.45	2.97	4.57	2.14	0.38	1.07	0.30
898	2	2.1	2.77	3.44	5.30	2.52	0.42	1.19	0.36
903	2.5	2.5	0.93	3.47	5.44	2.59	0.29	1.09	0.37
901	2.6	3.4	0.18	3.34	5.49	2.66	0.10	0.47	0.38

NOTE:
- Sludge Type A (Barrel 2)
- 500 cc leach solution - exposed to Cl_2 gas to raise solution Eh to 1164 MV.
- 2.2 gm sodium jarosite added as seed
- Temperature: 86-92^{o}C
- Raised pH at end of 2.5 hrs. to 3.4
- 4 gm $NaCO_3$/gm Fe
- Solution volume kept approximately constant

residue, Table 8.15. The initial rate of iron removal appears to be greatly enhanced when performed in the presence of the leach residue. However, these particular tests were performed at elevated solution Eh values and a large fraction of the chromium was also precipitated, i.e., 83% and 86%. This effect will be discussed under the sub-section (8.9) on oxidizing environments. Copper and aluminum shows a decrease because of the formation of insoluble phosphates (see Section 6.1).

Similar conclusions hold when considering larger scale testing, e.g., sodium jarosite precipitation from ten liters of solution showed 58% iron removal in about 2.5 hours (Table 8.16) while in-situ precipitation showed 88% (Table 8.17) iron removal in the same time period. Chromium loss to the solids, however, showed a different result, i.e., for the precipitation from solution only about 15% chromium loss occurred but in the in-situ precipitation about one-half was lost to the solids (no external oxidizing reagent was supplied to either of these precipitations). The chromium, copper, and aluminum losses are a result of the formation of relatively insoluble phosphates.

Filterability of a leach residue product and a jarosite-leach residue product is grossly different, i.e., filterability of a leach residue in a filter press is extremely difficult (4.5 $kg/m^2/hr.$) while filterability of a leach residue-jarosite product is much faster (22-55 $kg/m^2/hr.$) Qualitative test results are presented in Table 8.18. Another factor that is important for filterability is initial iron content. This effect is noted in the results of a series of tests presented in Tables 8.19. and 8.20. In actuality the formation of a poor filtering product at high iron content is most likely due to the rate of addition of reagents rather than the initial iron level. The conclusion of Dutrizac(1) is that jarosite can be effectively produced in solution containing 0.25-3.0 M Fe^{+3}.

The choice of the precipitating alkali cation can be Na^+, K^+, or NH_4^+. Precipitating testwork has been performed using each of the cations. Potassium was chosen for the large scale test (but any of the three cations would be appropriate) because according to Dutrizac(1) it forms the most stable

TABLE 8.15. REMOVAL OF IRON DURING IN-SITU LEACHING

Sample	Reaction Time (Hrs.)	Solution pH	Concentration in Solution (gpl)						
			Fe	Cu	Zn	Ni	Cr	Al	Cd
899	1	1.84	0.85	3.20	6.44	2.87	0.27	1.91	0.40
902	2.5	2.57	0.19	2.52	5.27	2.39	0.10	1.06	0.33
904	2.6	3.12	0.17	2.82	6.01	2.83	0.08	0.69	0.38

NOTE:
- Sludge Type A (Barrel 2)
- 200 gm sludge @ 23.7% solids in 250 cc leach solution containing 23.7 gm H_2SO_4. Leached for one-half hour at 85°C before jarosite ppt was initiated by adding $NaCO_3$.
- 4 gm $NaCO_3$/gm Fe
- Cl_2 added to raise Eh to 824 M.V. before $NaCO_3$ added
- Starting solution composition (gpl):
  8.6 Fe, 3.8 Cu, 5.8 Zn, 2.7 Ni, 0.58 Cr, 1.4 Al, 0.4 Cd

TABLE 8.16. JAROSITE PRECIPITATION FROM CONCENTRATED LEACH SOLUTION: TEN LITER TEST

gpl	Condition	Concentration in Solution (gpl) and Extraction from Solution (%)													
		Fe		Cu		Cr		Ni		Zn		Cd		Al	
		gpl	% Ext	gpl	% Ext	gpl	% Ext	gpl	% Ext	gpl	% Ext	gpl	% Ext	gpl	% Ext
980	Starting solution pH adjusted to 2.6	13.46		2.55		1.38		4.91		9.82		0.48		5.59	
981	40 minutes	7.52		2.10		1.05		3.94		7.96		0.37		4.51	
982	105	5.44		1.93		0.98		3.83		7.61		0.36		4.10	
983	140	3.60		1.54		0.73		3.01		6.00		0.28		3.20	
984	165	4.21		1.90		0.87		3.61		7.22		0.34		3.03	
985	Final (pH = 2.92)	5.71	57.6	2.48	2.7	1.17	15.2	4.74	3.5	9.62	2.0	0.45	6.2	5.07	9.3

NOTE:
- ·Sludge type A (Barrel 5) leached 30 minutes under standard conditions at 82°C. Solids removed and solution (10ℓ) reheated to 94°C
- ·134 gm $NaCO_3$ added and pH adjusted to 2.6
- ·Sample pulled as a function of time, volume of solution adjusted approximately to starting level before sampling. Time samples, therefore, not considered precise.
- ·Volume adjusted during test period using water at pH = 2.6.
- ·25 gm jarosite seed added

TABLE 8.17. JAROSITE PRECIPITATION IN-SITU DURING LEACH PROCESS: TEN LITER TEST

Sample	Condition		Concentration in Solution (gpl)						
	Time (min.)	pH	Fe	Cu	Cr	Ni	Zn	Cd	Al
	Leach								
969	40	1.5	8.35	1.68	0.90	3.22	6.49	0.31	3.74
	Jarosite Precipitation								
970	25	2.6 (Adjusted)	3.07	1.52	0.65	3.15	6.31	0.31	2.93
971	70	2.7 (Adjusted)	2.48	1.56	0.55	3.01	6.19	0.28	2.88
972	100	2.8 (Adjusted)	1.06	1.85	0.49	3.75	7.70	0.36	2.74
973	130	2.7 (Adjusted)	1.31 1.37	2.55 2.76	0.66 0.71	5.46 5.69	11.00 11.53	0.54 0.52	3.64 3.07
974	165	2.7 (Adjusted)	0.98	2.19	0.51	4.40	9.07	0.42	3.07
975	185	2.7	0.91	2.12	0.49	4.28	8.80	0.41	2.92

NOTE:
- Sludge type A (Barrel 5)
- 5000 gm sludge leached 40 minutes under standard conditions before jarosite reagents added
- 10 liters solution, 137 gm $NaCO_3$, temperature 94°C
- Sample pulled as function of time, volume of solution adjusted approximately to starting level before sampling. Time samples, therefore, not considered precise.
- Volume adjusted during test period using water at pH = 2.6

TABLE 8.18. POTASSIUM JAROSITE IN-SITU PRECIPITATION INTO LEACH RESIDUE: RESULTS AND QUALITATIVE COMPARSION OF FILTERABILITY

Sample No.	Condition	Concentration (gpl)							pH	Filterability
		Fe	Cu	Cr	Ni	Zn	Cd	Al		
1228	Starting Solution: Standard one-half hour leach	15.96 $[Fe^{++}]$=1.3 gpl	5.46	1.00	2.83	8.45	0.39	6.23	2.1	-----
1230	Four hour exposure	1.74 $[Fe^{++}]$= 1.3 gpl	4.36	0.62	2.50	7.22	0.34	4.84	1.7	Very Fast
	Series Repeat									
1229	Starting Solution	14.34	4.97	0.85	2.24	6.80	0.31	5.28	2.2	------
1231	Four hour exposure	2.01 $[Fe^{++}]$= 1.3 gpl	4.58	0.62	2.30	6.81	0.31	4.70	1.7	Very Fast
	Comparative Leaches									
1233B	One half hour leach for filter comparsion	14.81 $[Fe^{++}$ = 0.7 gpl	4.89	0.83	2.43	7.05	0.35	4.87	1.0	Very Slow
1234	Repeat of 1233B	12.16 $[Fe^{++}$ = 0.7 gpl	4.91	0.64	2.44	7.28	0.34	5.06	1.0	Very Slow

Notes:
- Sludge barrel 2 leached one half hour under standard conditions(pH = 1.0) then jarosite conditions established.
- Filter comparsion conducted on a four inch water aspirator filter. Qualitative filter rates are:
  very fast - entire 900cc of leach solution cleaned of solids in <5 minutes;
  very slow - entire 900cc of leach solution cleaned of solids in >1 hour and several replacements of the filter paper required.

TABLE 8.19. POTASSIUM JAROSITE IN SITU PRECIPITATION: COMPARISON OF STARTING IRON CONTENT IN LEACH SOLUTION

Sample	Condition	Concentration (gpl)							Filterability
		Cu	Fe	Zn	Cr	Ni	Cd	Al	
	15 gpl Fe Solution								
2322	Starting Solution	5.45	14.96	6.24	6.45	1.63	0.08	0.27	
2325	Final Solution, 6 hr.	4.24	0.95	6.01	3.43	1.76	0.08	0.10	Poor
	10 gpl Fe Solution								
2318	Starting Solution	3.55	10.31	4.21	1.42	1.09	0.04	0.18	
2321	Final Solution, 6 hr.	3.62	0.33	4.71	3.36	1.36	0.05	0.13	Excellent
	5 gpl Fe Solution								
2314	Starting solution	1.73	5.60	2.31	2.41	0.61	0.02	0.09	
2317	Final Solution, 6 hr.	2.12	0.12	2.77	1.64	0.77	0.02	0.06	Excellent

NOTE:
- Each leach solution produced by varying the solid (Barrel 18)/liquid ratio during the leach, 1/2 hr., 20^{0}C, acid content was 100 w/o of solid weight.
- Jarosite Conditions: >90^{0}C, 6 hrs., 1 gm K_2SO_4/gm Fe, solution oxidized with H_2O_2 (30%) during last two hours of test, pH maintained 2.5 with KOH.
- The 15 gpl test solution pH overshot to 3.3. Probable reason for high loss of copper in final jarosited solution and for the poor filterability.

TABLE 8.20. POTASSIUM JAROSITE PRECIPITATION OF IRON AS A FUNCTION OF IRON CONCENTRATION IN STARTING SOLUTION

Sample #	Conditions	Concentration in Solution (gpl)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
1056	Starting Solution	19.40	5.07	5.53	1.53	15.34	0.71	8.22
1160	4 Hr. Exposure (unfilterable)	---	---	---	---	---	---	---
1161	Starting Solution	10.91	2.58	3.53	3.87	7.39	0.32	5.05
1165	4 Hr. Exposure	6.09	2.76	4.12	4.21	8.25	0.37	5.41
		↑ [Fe^{++}] = 4.83 gpl						
1166	Starting Solution	4.55	1.73	1.89	12.67	3.03	0.13	2.05
1167	4 Hr. Exposure	2.66	1.62	1.84	11.87	2.90	0.12	1.91
		↑ [Fe^{++}] = 1.40 gpl						

NOTES:
- Leach solutions from standard leach on barrel 2 material; 1166 sample doped with high chromium leach solution from barrel 8 material.
- 750 cc solution adjusted to pH ≈2.0.
- 21 gm seed.
- Temperature: 90°C.
- Final solids washed on filter pad. Extensive washing not performed.
- One gm K_2SO_4/gm Fe.

jarosite. The present work indicates a faster rate of iron removal using potassium, Tables 8.21. and 8.22. Additional jarosite precipitation data summary tabulations are presented in Tables 8.23.-8.25., i.e.,

- Potassium jarosite In Situ Precipitation into Leach Residue: (Table 8.23).
- In-situ potassium jarosite precipitation at initial pH = 3 (Table 8.24).
- Comparative iron oxidation and jarosite in-situ precipitation (Table 8.25).

8.3.1.2. Large Scale Testwork

Solution iron content can be effectively lowered to the range of several hundred parts per million by potassium jarosite precipitation. It would be desirable to have a lower value but lower concentrations do not appear to be achievable in large scale testwork. The presence of several hundred parts per million iron is not a major problem because it will be coextracted with zinc during solvent extraction; will not contaminate the zinc strip solution because it will not be stripped by 200 gpl H_2SO_4; and can be stripped from an organic bleed stream to rejuvenate the organic.

Detailed results for five large scale sequential tests are presented in Section 8.14. A summary of metal value loss from leach solutions are presented in Table 8.26; 5-7 hours of precipitation time resulted in 94.4-99.5% iron removal; 10.6-13.3% copper loss, 0-5.6% nickel loss, 25.0-42.8% chromium loss, 0-2.5% zinc loss, and 1.9-29.3% aluminum loss. A portion of the metal value loss is recoverable by acid leaching. This was demonstrated by leach tests performed on the jarosite product from sequential test series five. The composition of the jarosite residue is presented in Table 8.27. and the results of leach tests on the residue are presented in Table 8.28. Three fourths of the copper is recoverable, two-thirds of the zinc, 18.8% of the chromium and 100% of the nickel by an acid leach (pH = 0.5).

TABLE 8.21. JAROSITE PRECIPITATION OF IRON FROM A NOMINAL TEN GPL IRON SOLUTION (OXIDIZED)

Sample #	Condition	Concentration (gpl)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
1177	Starting Solution	11.53	3.09	3.95	3.05	7.26	0.30	4.64
1181	NH_4^+, 4 Hours	5.28	3.15	4.18	2.95	7.67	0.30	4.63
1182	Na^+, 4 Hours	9.80	2.82	3.61	2.81	6.55	0.26	4.13
1183	K^+, 4 Hours	2.39	2.70	3.61	2.41	6.70	0.28	4.08
1189	Starting Solution	10.90	3.40	4.72	3.28	7.94	0.39	4.85
1190	NH_4^+, 4 Hours	5.23	3.35	4.79	3.07	7.93	0.40	4.65
		↑ $[Fe^{++}]$ = 0.09 gpl						
1187	Starting Solution	11.22	3.27	4.50	3.21	7.70	0.37	4.78
1188	K^+, 4 Hours	3.01	3.30	4.93	3.01	8.27	0.42	4.76
		↑ $[Fe^{++}]$ = 0.07 gpl						

NOTE:
- ·Leach solution from barrel 2 material.
- ·750cc of solution, pH adjusted initially to 2.0.
- ·21 g seed test.
- ·1 gm reagent/1 gm Fe.
- ·Temperature = 90°C.
- ·50 cc of 30% H_2O_2 added to each test sample.

TABLE 8.22. JAROSITE PRECIPITATION OF IRON AS A FUNCTION OF TIME: NH_4^+, K^+

Sample #	Conditions	Concentration in Solution (gpl)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
1077	Starting Solution	25.00	8.67	7.42	2.86	16.63	1.04	6.93
	NH_4^+ Test							
1108	1 Hr.	17.14	8.28	6.91	2.66	16.97	0.99	6.94
1110	2 Hrs.	13.98	7.90	6.66	2.48	16.12	0.95	5.54
1112	3 Hrs.	11.27	6.91	5.84	2.16	14.08	0.83	5.65
1114	4 Hrs. (final after filtering)	12.84 †[Fe^{++}] = 7.7 gpl	8.43	7.15	2.61	17.07	1.03	6.87
	K^+ Test							
1109	1 Hr.	14.19	8.39	7.31	2.68	17.43	1.04	6.88
1111	2 Hrs.	10.93	8.18	7.18	2.56	17.05	1.02	6.67
1113	3 Hrs.	9.18	7.93	7.00	2.44	16.52	0.99	6.50
1115	4 Hrs. (final after filtering)	8.26 †[Fe^{++}] = 7.7 gpl	8.07	7.09	2.44	16.81	1.01	6.61

NOTES:
- ·Leach solution from standard leach on barrel 2 material.
- ·750 cc, pH = 2 (initial).
- ·Approximately 50 gm. seed, source of seed was from 1092 (for NH_4^+), 1093 (K^+)
- ·Temperature: 85-92°C.
- ·Final filtering included washing with pH 2 water. This was not extensive washing, only enough added to recover solution to initial 750 cc value.

TABLE 8.23. POTASSIUM JAROSITE IN-SITU PRECIPITATION INTO LEACH RESIDUE: INCREMENTAL INCREASE IN PH.

Sample	Condition	Concentration (gpl)							pH
		Fe	Cu	Cr	Ni	Zn	Cd	Al	
1258	Starting Solution: Standard 1/2 hr. leach	11.51	3.33	0.62	1.53	4.95	0.21	4.52	
		$[Fe^{++}] = 0.5$ gpl							
1259	2 hr. exposure Initial pH = 1.5	3.03	3.12	0.53	1.54	4.98	0.21	4.43	Initial = 1.52 Final = 1.28
		$[Fe^{+2}] = 0.05$ gpl							
1260	2 additional hours exposure, initial pH = 2.0	0.70	3.53	0.54	1.79	5.74	0.25	4.77	
		$[Fe^{++}] = 0.1$ gpl							
1261	2 additional hours exposure, initial pH = 3.25	0.33	4.57	0.58	2.40	7.77	0.33	4.77	Initial = 3.25 Final = 2.66
		$[Fe^{++}] = 0.2$ gpl							

NOTE: ·Barrel 2 sludge leached under standard conditions for one-half hour then conditions changed to favor jarosite precipitation; i.e., T = 88-92^{0}C, 1 gm K_2SO_4/gm Fe, 25cc of 30% H_2O_2 added slowly.

TABLE 8.24. IN-SITU POTASSIUM JAROSITE PRECIPITATION AT AN INITIAL PH = 3

Sample	Condition	Concentration (gpl)							Filterability
		Fe	Cu	Cr	Ni	Zn	Cd	Al	
1278	Starting Leach (1/2 hr.) pH = 2.0	9.20	2.97	0.50	1.20	4.18	0.18	3.92	
1281	6 hr. exposure to jarosite conditions @ pH = 3 (final pH = 2.5)	0.35	3.72	0.35	1.84	6.31	0.27	3.35	Excellent

NOTE: ·Barrel 2 sludge leached under standard conditions for one-half hour, then conditions changed to form jarosite precipitation.

·25cc of 30% H_2O_2 added slowly during test period.

·Temperature = 86-90°C.

·1 gm K_2SO_4/gm Fe.

TABLE 8.25. COMPARATIVE IRON OXIDATION AND JAROSITE IN-SITU PRECIPITATION

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Cr	Ni	Zn	Cd	Al
	Oxidation by $Cr_2O_7^=$							
1317	Starting Solution	8.86	2.88	0.53	1.31	4.47	0.19	3.78
		$[Fe^{++}] = 0.36$ gpl						
1318	Six hour exposure	0.14	2.54	0.61	1.31	4.48	0.13	2.49
		$[Fe^{++}] <$ D.L.						
	Oxidation by H_2O_2							
1319	Starting Solution	9.57	3.25	0.56	1.32	4.54	0.20	4.07
		$[Fe^{++}] = 0.28$ gpl						
1320	Six hour exposure	0.10	2.72	0.30	1.30	4.46	0.13	2.86
		$[Fe^{++}] = 0.024$ gpl						

Notes: . Barrel 2 sludge leached one half hour under standard conditions, then conditions established for potassium jarosite precipitation. Oxidant added dropwise beninning four hours after start of test; 1.5 g $K_2Cr_2O_7$ added per gram of iron, 25cc -30% H_2O_2/950cc solution.

TABLE 8.26. METAL VALUE LOSS DURING LARGE SCALE JAROSITE PRECIPITATION

Sample No.	Condition	Metal Value Precipitation (%)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
1371	Series One Sequential Test (Table 8.121) 5 Hr precipitation, starting Fe; 14.00 gpl.	99.5	13.3	0.0	25.0	0.8	0.0	1.9
2125	Series Three Sequential Test (Table 8.125) 6 Hr precipitation, starting Fe; 5.21 gpl.	95.6	10.6	4.5	42.8	0.0	0.0	15.2
2126	Series Four Sequential Test (Table 8.126) 6 Hr precipitation, after 8 hr settling.	96.3	12.7	5.6	41.0	2.5	0.0	21.3
2494	Serie Five Sequential Test (Table 8.127) 7 Hr precipitation, starting Fe; 9.73 gpl.	94.4	11.7	0.0	25.8	0.0	0.0	29.3

Note: . Detailed results presented in Section 8.13.

TABLE 8.27. JAROSITE RESIDUE FROM SEQUENTIAL TEST SERIES FIVE

Sample No.	Concentration in Solids (%)						
	Cu	Fe	Zn	Cr	Ni	Ca	K
2611	2.74	19.23	0.26	3.07	0.03	1.37	6.22
2649	2.80	19.55	0.27	3.17	0.04	1.21	6.41
2650	2.73	19.10	0.27	3.10	0.05	1.21	6.15
2651	2.88	20.47	0.29	3.33	0.03	1.22	6.45
2652	2.88	20.41	0.29	3.32	0.03	1.22	6.54
Average Composition	2.81±0.07	19.75±0.72	0.28±0.01	3.26±0.17	0.04±0.01	1.22±0.12	6.35±0.19

TABLE 8.28. RELEACH OF PRECIPITATED JAROSITE RESIDUE

Sample No.	Condition	Extracted From Solid (%)					
		Cu	Fe	Zn	Cr	Ni	Al
2611	Starting Solid Composition (Avg. Five samples)	2.81±0.07	19.75±0.72	0.28±0.01	3.26±0.17	0.04±0.01	1.50±0.06
2698	pH = 0.5 (Initial) pH = 0.7 (Final)	75.0	11.5	66.7	18.8	100.0	13.0
2701	pH = 1.5 (Initial) pH = 1.7 (Final)	25.0	5.9	33.3	1.2	0.0	2.0
2701	pH = 2.5 (Initial) pH = 3.4 (Final)	0.2	0.0	0.0	0.0	0.0	0.0

Notes:
. 10 g solid/100 cc solution, 25°C, 18 hour exposure.
. Sequential test series five jarosite solid chosen for releach study.

8.3.2. Iron Removal by Solvent Extraction

It has often been stated that practically all metallurgical flowsheets require a series of steps to successfully solve the problem of iron removal. It is true that in some mixed metal sludges iron is not an important constituent. If that is the case then the flowsheet presented in Figure 6.1. would be appropriate without the jarosite precipitation step. However, it is true that a plant that will be treating mixed metal sludge materials must have a way to reject iron. If the iron content is high (a solution is produced that contains several gpl Fe) then its segregation can be via the jarosite (or Geothite) process. However, the use of the jarosite precipitation process results in an iron bearing solution of a few hundred parts per million. Removal of the residual iron content is required. Removal can be accomplished by solvent extraction using one of two reagents, D_2EHPA or Versatic Acid. A major experimental investigation was conducted on low iron bearing solutions (that were not previously treated by jarosite precipitation). This study is discussed in Section 8.4. The content of this section will, therefore, be limited to iron and zinc coextraction from jarosited solutions by D_2EHPA. A short discussion will be presented using Versatic Acid.

D_2EHPA

Of the two reagents only D_2EHPA is being used commercially to extract iron from a solution, e.g., Tecnicas Reunidas uses a solvent extraction process to remove the iron from a zinc leach liquor at its Espindesa operation(34). Their flowsheet is presented in Figures 8.8. and 8.9.

The anticipated selectivity of D_2EHPA for iron is shown in a qualitative way in Figures 8.10a and 8.10b. The figure suggests that iron should be selectively extracted from other metal values at a pH 1 or iron and zinc should be co-extracted from the other metal values at pH$\sim$ 1.5.

D_2EHPA was investigated as an extractant for iron early in the present experimental study. A design matrix is presented in Table 8.29. The design matrix verify, on a small laboratory scale, the selectivity of D_2EHPA-Deconol-Kerosene mixtures for iron. This conclusion is further

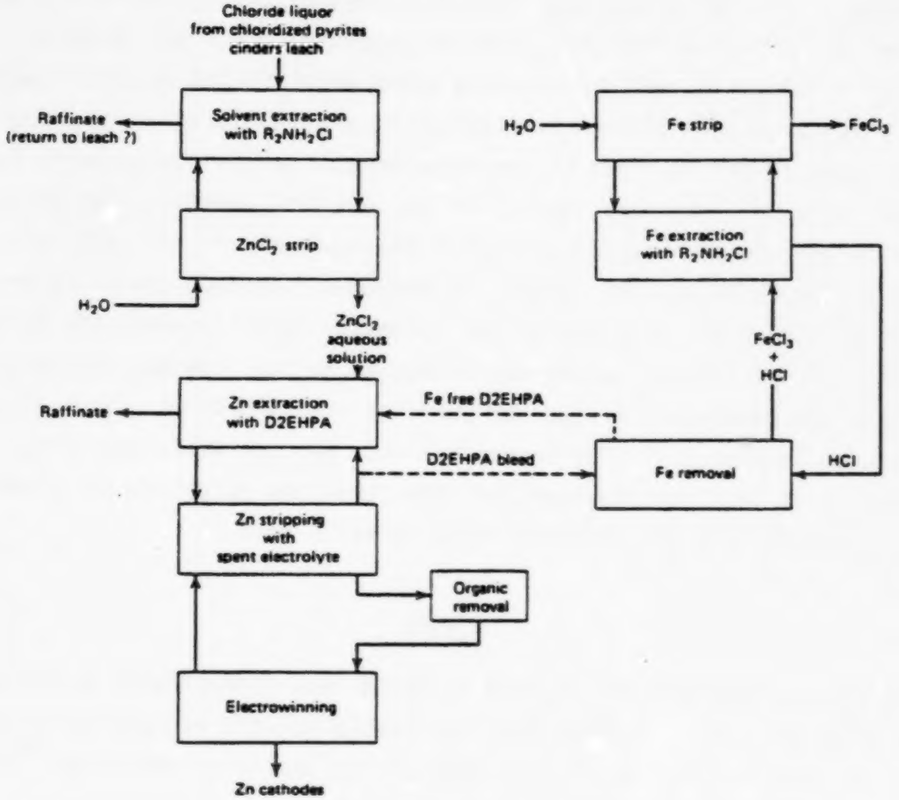

Chloride liquor from chloridized pyrites cinders leach
Raffinate (return to leach ?)
Solvent extraction with R_2NH_2Cl
$ZnCl_2$ strip
H_2O
$ZnCl_2$ aqueous solution
Raffinate
Zn extraction with D2EHPA
Fe free D2EHPA
D2EHPA bleed
Zn stripping with spent electrolyte
Organic removal
Electrowinning
Zn cathodes
H_2O
Fe strip
$FeCl_3$
Fe extraction with R_2NH_2Cl
$FeCl_3$ + HCl
Fe removal
HCl

Figure 8.8. Outline flowsheet for the Espindesa process. (From Flett(35))

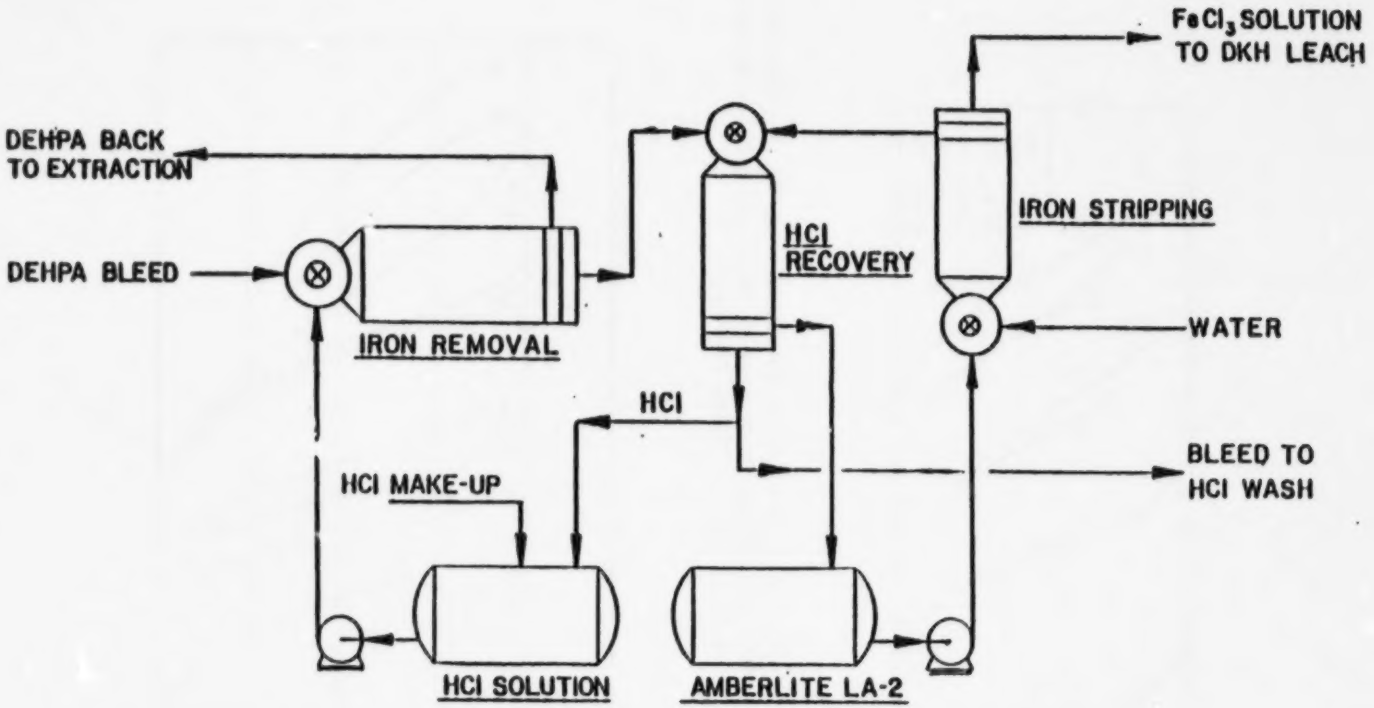

$FeCl_3$ SOLUTION TO DKH LEACH
DEHPA BACK TO EXTRACTION
IRON STRIPPING
HCl RECOVERY
DEHPA BLEED
WATER
IRON REMOVAL
HCl
BLEED TO HCl WASH
HCl MAKE-UP
HCl SOLUTION
AMBERLITE LA-2

Figure 8.9. Auxiliary facility for iron removal from D_2EHPA. (From Nogueria(34))

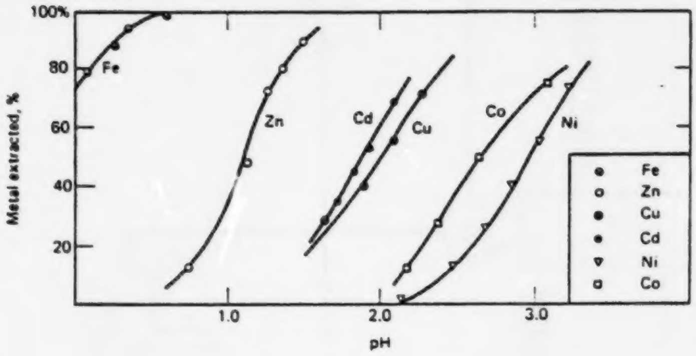


Figure 8.10a. Equilibrium distribution for metals in 30% D$_2$EHPA-Shellsol System. Extraction from single metal sulfate solutions of 5 g/liter metal. (From Thorsen(30)).

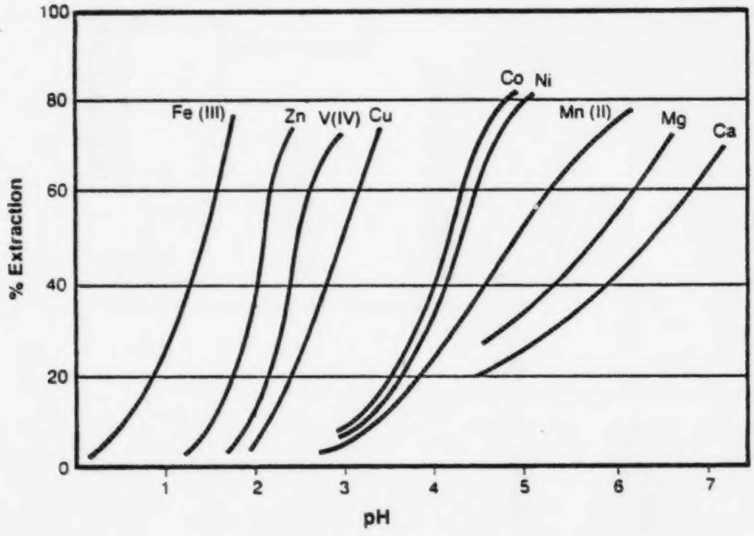


Figure 8.10b. Influence of pH on zinc extraction by **D$_2$EHPA**. (From Henkle(30))

TABLE 8.29. DESIGN MATRIX FOR D_2EHPA EXTRACTION OF IRON FROM SLUDGE LEACH SOLUTION (1/8 REPLICA)

Results: Extraction from Solution (%)

Sample		DEHPA (%)	Type Kerosene	Decanol (%)	Mix Time (min.)	Mix Temp. (°C)	Leach Solution pH							
	Base	20	KERMAC 470-B	10	2	40	1.70							
	Unit	5	---	10	1	15	0.20							
	High (+)	25	470-B	20	3	55	1.90							
	Low (-)	15	450	0	1	25	1.50							
	Test No.								Cu	Fe	Cr	Ni	Zn	Cd
323	1	-	-	-	-	-	-		0	10.2	0	0	11.1	0
324	2	+	-	-	+	-	+		0	71.3	0	0	4.8	0
330	3	-	+	-	+	+	-		0	469 333	0	0	2.9 (3.3)	0
331	4	+	+	-	-	+	+		0	33.3	0	0	3.5	0
332	5	-	-	+	+	+	+		0	45.4	0	0	0	0
333	6	+	-	+	-	+	-		0	42.1	0	0	0	0
335	7	+	+	+	+	-	-		0	0	0	0	0	0
326	8								0	10.0	0	0	0	0
327	Base								0	22.6	0	0	2.0	0
								Max. Exp. Variable	±4.3%	±7.5%	±6.1	±5.0	±5.5	±1.0
Effects														
	Cu	0	0	0	0	0	0							
	Fe	+6.8	-9.8	-8.0	+11.0	9.5	5.1							
	Cr	0	0	0	0	0	0							
	Ni	0	0	0	0	0	0							
	Zn	-0.7	-1.2	-2.8	-0.9	-1.2	-0.7							
	Cd	0	0	0	0	0	0							

NOTE:
- Sludge Type A
- Initial Solution Composition (gpl): 0.04 Cu, 3.90 Fe, 0.49 Cr, 2.24 Ni, 0.21 Cd
- Organic/Aqueous = 1; 50 cc each
- Test 5 Duplicated
- Observations on Phase Separation Presented in Appendix Table 8.27.

TABLE 8.30. OBSERVATIONS ON PHASE SEPARATION: DESIGN MATRIX TESTS (TABLE 8.29) FOR IRON REMOVAL USING D_2EHPA

Test #	Observations
1	Some Muck*
2	Poor Separation, Very Mucky
3	Good Separation
4	Fair Separation
5	Poor Separation, Very Mucky
5b	Some Muck
6	Good Separation
7	" "
8	" "
Baseline A	" "
Baseline B	" "
Baseline C	" "

*Muck = A layer of organic-aqueous that disappears slowly.

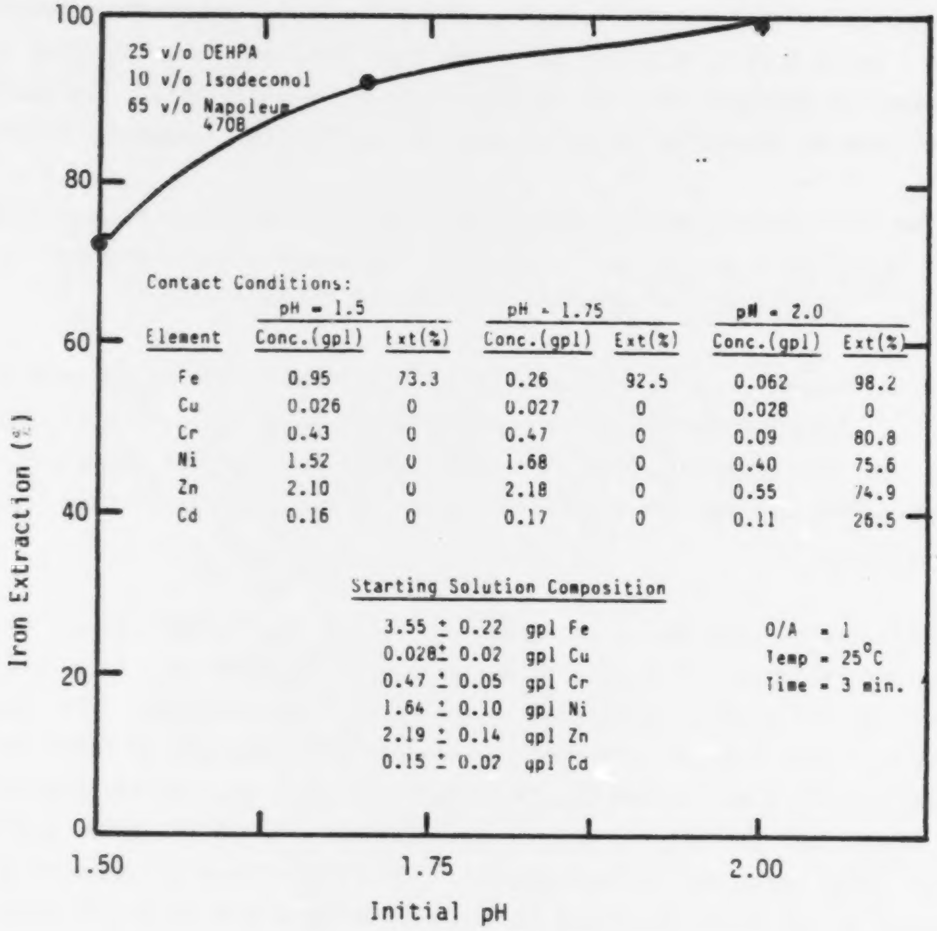
substantiated by data presented in Figure 8.11 depicting the influence of pH on iron extraction for a single contact shake test. A large number of extraction shake tests were conducted and the results are reported in Section 8.3.3.

The extraction study was followed by a study of the stripping characteristics of the organic phase. The strip tests immediately showed that ferric iron is very effectively extracted from the leach solution using D_2EHPA but cannot be stripped from the organic phase by sulfuric acid. The detailed results from an extensive series of tests are presented in Appendix 8.3.3.

The conclusion from the testwork is that iron cannot be stripped from D_2EHPA by sulfuric acid. This result is in agreement with literature sources(35) but is not in agreement with patents by Reinhardt(36).

Iron, however, can be effectively stripped from D_2EHPA by hydrochloric acid(34). Experimental results are presented in Table 8.31. The ability to strip iron (and aluminum) from the organic phase means active reaction sites can be regenerated and the organic phase can be recycled for further iron and zinc pick-up.

Zinc can be stripped in preference to iron from a D_2EHPA organic phase using sulfuric acid. This result is presented in Table 8.32., i.e., zinc is effectively stripped by sulfuric acid but iron is not stripped. The importance of the fact that iron and zinc bearing organic solutions can be selectively stripped of its zinc content by use of sulfuric acid and then stripped of its iron content by hydrochloric acid is that solvent extraction can be applied to a mixed metal solution (including iron). This fact allows an appropriate treatment scheme to be developed for iron-chromium sludge materials without using a jarosite precipitation unit operation: i.e., for a high chromium bearing sludge the treatment sequence would be: leach; SX of copper from the aqueous phase with an oxime reagent; SX of iron and zinc from the aqueous phase using D_2EHPA; selective stripping of zinc from the organic phase by sulfuric acid followed by stripping of iron from the organic phase by hydrochloric acid solution.



Contact Conditions:

	pH = 1.5		pH = 1.75		pH = 2.0	
Element	**Conc.(gpl)**	**Ext(%)**	**Conc.(gpl)**	**Ext(%)**	**Conc.(gpl)**	**Ext(%)**
Fe	0.95	73.3	0.26	92.5	0.062	98.2
Cu	0.026	0	0.027	0	0.028	0
Cr	0.43	0	0.47	0	0.09	80.8
Ni	1.52	0	1.68	0	0.40	75.6
Zn	2.10	0	2.18	0	0.55	74.9
Cd	0.16	0	0.17	0	0.11	26.5

Starting Solution Composition

3.55 ± 0.22 gpl Fe
0.028 ± 0.02 gpl Cu
0.47 ± 0.05 gpl Cr
1.64 ± 0.10 gpl Ni
2.19 ± 0.14 gpl Zn
0.15 ± 0.07 gpl Cd

O/A = 1
Temp = 25°C
Time = 3 min.

Figure 8.11. Influence of pH on iron extraction by D_2EHPA.

TABLE 8.31. FERRIC IRON STRIPPING FROM D_2EHPA WITH HCL

Sample No.	Condition	Concentration (gpl)						
		Fe	Zn	Cu	Cr	Ni	Cd	Al
1322	Starting Solution	4.09	2.85	1.16	0.29	1.04	0.14	1.54
	Iron Loading							
1323	Contacted with DEHPA (20 v/o); O/A = 2, 40°, pH = 2.18	0.32	1.75	1.15	0.28	1.04	0.14	1.37
	HCl Stripping							
1325A	Contacted with 4N HCl; O/A = 0.5, 40°C	0.80	0.26	0.004	0.002	< D.L	< D.L	0.043
1325B	Repeat	0.88	0.31	0.008	0.003	0.001	< D.L.	0.053
	Strip Recovery (%)							
1325A		85	94	---	---	---	---	100
1325B		94	100	---	---	---	---	100

Notes: . All concentrations reported for the aqueous phases.

TABLE 8.32. BENCH SCALE SEQUENTIAL SOLVENT EXTRACTION TESTWORK: COPPER AND ZINC REMOVAL

Sample No.	Condition	Concentration (gpl in Aqueous Phase)						
		Cu	Fe	Zn	Ni	Cr	Cd	Al
1466	Jarosited (Barrel 14) Leach Solution	3.14	1.44	9.37	4.95	0.54	0.52	1.58
1467	Diluted 1466, pH = 1.75	1.56	0.69	4.99	2.75	0.27	0.24	0.63
	Cu SX							
1468	LIX 622 (10 v/o) contacted with 1467 (O/A = 1)	0.02	0.69	5.00	2.74	0.27	0,25	0.64
1469	LIX 622 (10 v/o) contacted with aqueous from 1468 (O/A = 1). Initial pH of aqueous adjusted to 1.75	0.004	0.68	4.93	2.71	0.26	0.25	0.63
	Zn SX: DEHPA (30 v/o)							
	Extraction							
1470	Aqueous 1469 adjusted to pH = 2; then contacted (first contact) with DEHPA organic (O/A = 1)	0.001	0.63	1.71	2.76	0.27	0.23	0.55
1475	Aqueous 1470 adjusted to pH = 2; then re-contacted (2nd contact) with DEHPA Organic (O/A = 1)	< D.L.	0.57	0.32	2.74	0.27	0.19	0.39

TABLE 8.32. CONTINUED

Sample No.	Condition	Concentration (gpl in Aqueous Phase)						
		Cu	Fe	Zn	Ni	Cr	Cd	Al
1477	Aqueous 1475 adjusted to pH = 2; then recontacted (3rd contact) with DEHPA organic (O/A = 1)	< D.L.	0.44	0.03	2,59	0.25	0.12	0.16
1479	Aqueous 1477 adjusted to pH = 2; then recontacted (4th contact) with DEHPA organic (O/A = 1)	< D.L.	0.35	< D.L.	2.75	0.27	0.05	0.04
	DEHPA Organic Strip							
1471	Organic 1470 (1st extraction contact) stripped with 200 gpl H_2SO_4	< 1 ppm	< 0.01	3.50	< 0.01	< 0.01	0.02	0.01
1473	Above organic (1471) stripped second time with 200 gpl H_2SO_4	< 1 ppm	< 0.01	0.01	< D.L.	< D.L.	< D.L.	< 0.01
1472	Organic 1470 (1st extraction contact) stripped with 150 gpl H_2SO_4	< 0.01	< 0.01	3.36	< 0.01	< 0.01	0.02	< 0.01
1474	Above organic (1472) stripped second time with 150 gpl H_2SO_4	< 1 ppm	< D.L.	0.01	< D.L.	< D.L.	< D.L.	< 0.01

TABLE 8.32. CONTINUED

Sample No.	Condition	Concentration (gpl in Aqueous Phase)						
		Cu	Fe	Zn	Ni	Cr	Cd	Al
1476	Organic 1475 (2nd extraction contact) stripped with 200 gpl H_2SO_4	< 1 ppm	0.01	1.39	0.01	<0.01	0.04	0.04
1477	Organic 1477 (3rd extraction contact) stripped with 200 gpl H_2SO_4	< D.L.	< 0.01	0.26	<0.01	<0.01	0.05	0.05
1480	Organic 1479 (4th extraction contact) stripped with 200 gpl H_2SO_4	< 1 ppm	< 0.01	0.03	0.02	<0.01	0.07	0.02

Notes: . All concentrations are given for the aqueous phase after the designated contact.
. O/A = 1, Ambient temperature, contact for 3 minutes for all tests.
. 500 cc of solution contacted.

Iron can also be stripped from D_2EHPA by use of a reductive stripping technique modeled after reduction stripping used in industrial uranium recovery(37). The results are presented in Section 8.3.3. This technique results in adding iron to the strip solution and, therefore, requires that a disposal technique be developed for the strip (H_2SO_4) solution. The reader is referred to Appendix 8.3.3.7. if interested in details of the study.

VERSATIC ACID

Potentially iron can be removed by solvent extraction from an acid solution by Versatic 911 - kerosene mixtures. An equilibrium distribution diagram is presented in Figure 8.12. A selective separation of iron from Cu, Cd, Ni, Zn appears possible using Versatic 911 as the extracting reagent. The selectivity for iron requires the pH to be approximately 2.5. The problem with this approach is that the iron product must be further treated, i.e., a solution of ferric sulfate is produced by sulfuric acid stripping or a solution of ferric chloride is produced by hydrochloric acid stripping. The advantage of the previously discussed jarosite process over solvent extraction is that a readily disposable solid product is produced in the jarosite precipitation. Thorsen(30) and Teireira(38) has described a process for stripping Versatic acid of its iron content by a process called hydrolytic stripping; see Figure 8.13. The advantage of the procedure is that solid Fe_2O_3 is produced. The disadvantage of the process is that the stripping operation must be conducted under autoclave conditions.

Experimental work was not performed in the present study using Versatic Acid for iron removal nor is such a process presently used commercially.

8.3.3. Support Data: D_2EHPA Load/Strip Testwork. Summary of Testwork on Fe + Zn Extraction

8.3.3.1. Fe Extractions: Solution Preparation

The initial goal of this experimental work was to extract iron from copper-free raffinate using D_2EHPA in 470B. A batch of leach solution (14 l) was prepared for this study by the standard method, and then copper was

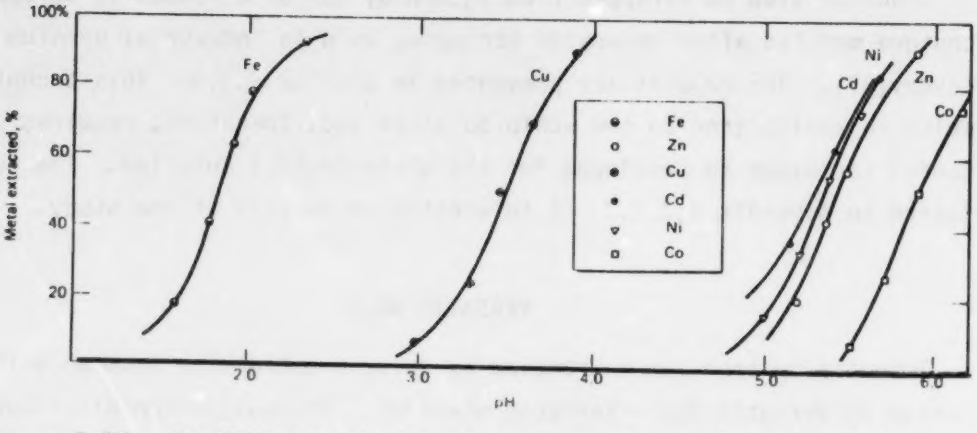
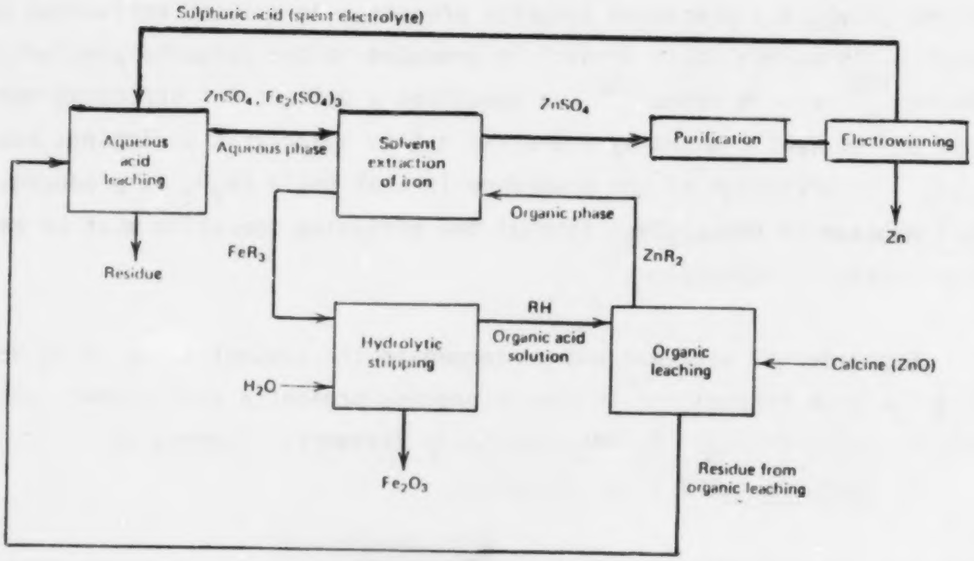


Figure 8.12. Equilibrium distribution for metals in 30% VERSATIC 911-Shellsol system. Extraction from single metal sulfate solutions of 5 g/liter metal. (From Thorsen[30]).



Sulphuric acid (spent electrolyte)
$ZnSO_4$, $Fe_2(SO_4)_3$
Aqueous acid leaching
Aqueous phase
Solvent extraction of iron
$ZnSO_4$
Purification
Electrowinning
Zn
Organic phase
Residue
FeR_3
ZnR_2
RH
Hydrolytic stripping
Organic acid solution
Organic leaching
Calcine (ZnO)
H_2O
Fe_2O_3
Residue from organic leaching

Figure 8.13. Schematic flowsheet of integrated organic leach and solvent extraction process in zinc hydrometallurgy. (From Thorsen[30]).

extracted in the full scale SX unit. Copper was extracted in two stages using LIX-622 at 15 v/o, and stripped in one stage with 200 gpl acid. This technique satisfactorily removed selectively the copper (Table 8.33).

The test provided operating experience with the large SX unit.

8.3.3.2. Fe Extractions: Influence of pH

Samples of the leach solution were adjusted to four pH values, 1.4, 1.6, 1.8, 2.0. They were then contacted for three minutes at an organic/aqueous ratio of one using 25% D_2EHPA in KERMAC 470B kerosene at room temperature. When carried out at this low temperature the extractions were quite good (as indicated by pH change), but the phase separations were slow. By heating the flasks to 38°C and re-mixing, the separations became rapid (less than two minutes). The tests were qualitatively examined by determining the change in pH that occurred in each contactor. These changes are indicated below. The pH values at 38°C indicate that little additional loading occurred during the second three minute shake period.

Original pH	Final pH at 25°C	Final pH at 38°C
1.4	1.28	1.28
1.6	1.32	1.32
1.8	1.35	1.35
2.0	1.41	1.41

The pH changes were converted to ΔH^+ and plotted in the graph below, which indicates an abrupt increase in extraction at pH 1.8.

Experimental extraction data are presented in Table 8.34. Iron is very effectively extracted at all pH values.

TABLE 8.33. FIRST LARGE SYSTEM (1 GALLON MIXER-SETTLER) TEST FOR COPPER EXTRACTION USING LIX 622

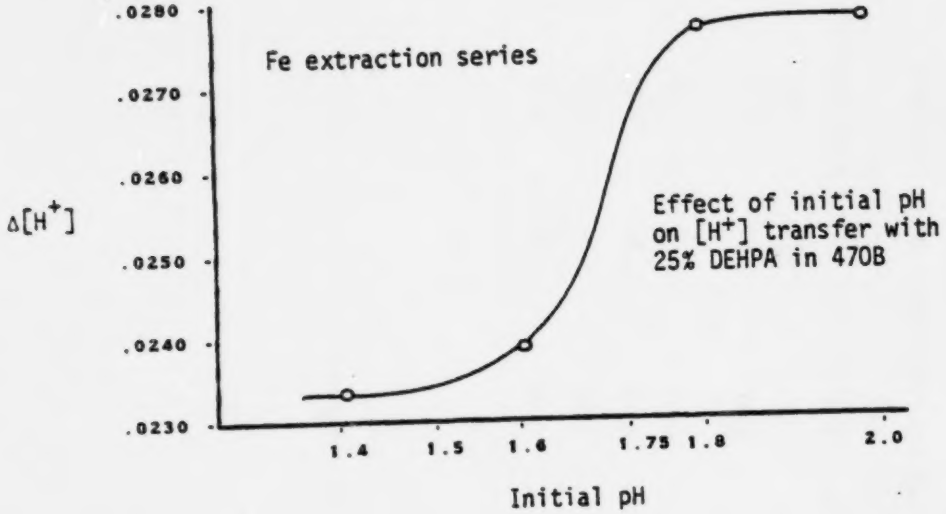
Conditions: 15 v/o LIX 622
85 v/o KERMAC 470B
Two Stages of Extraction
One Stage of Strip
pH of Leach Solution into System: 1.75
Temperature : 25°C
Solution Flow Rate : 250 cc/min.
Total Volume Treated : 14 liters
Strip Acid : 200 gpl H_2SO_4

	Cu	Fe	Ni	Zn	Cr	Cd
Original Feed (gpl)	2.73	6.10	1.90	4.04	0.42	0.24
Raffinate (gpl)	0.043	6.14	1.94	4.12	0.42	0.25

TABLE 8.34. D_2EHPA EXTRACTION FROM SLUDGE LEACH SOLUTIONS (COPPER FREE) AS A FUNCTION OF PH

Sample	pH		Concentration in Solution (gpl) after Organic Contact					
	Start	Final	Fe	Zn	Cr	Ni	Cd	Al
589 (Starting Solution)			6.18	4.34	0.41	2.00	0.27	1.05
585	1.40	1.28	0.18	3.73	0.37	1.83	0.25	0.94
586	1.60	1.32	0.11	3.67	0.38	1.90	0.26	0.93
587	1.80	1.35	0.08	3.39	0.36	1.78	0.24	0.89
588	2.00	1.41	0.08	3.68	0.39	1.97	0.26	0.94

NOTE: ·Organic: 25 v/o DEHPA
75 v/o KERMAC 470B
·Contact Time: 3 min.
·Temperature: 25°C
·O/A = 1, 50cc each



8.3.3.3. Fe Extraction: Influence of D_2EHPA Content

Cu free raffinate (pH = 1.75) was contacted with an organic/aqueous ratio of one at 40°C with 25, 30, 35, and 40% D_2EHPA in 470B. Final raffinate pH values were 1.41, 1.36, 1.34, and 1.35, indicating that 30% D_2EHPA was probably sufficient to pick up most of the Fe^{+++}, Table 8.35.

Two of the tests (25% and 40%) were repeated holding the pH constant during the extraction by adjusting back to 1.75 after one minute of contact.

8.3.3.4. Fe Extraction: Stripping Series

The data obtained in the influence of pH test series and in earlier work indicated that Fe could easily be extracted, perhaps not to 0 gpl in raffinate, but at least to less than 1 gpl. It was assumed that 25% D_2EHPA at 40°C,

TABLE 8.35. INFLUENCE OF DEHPA CONCENTRATION ON EXTRACTION FROM SLUDGE LEACH SOLUTION (COPPER FREE) AT PH = 1.75

Sample	DEHPA	Concentration in Solution After Organic Contact (gpl)						Final pH
		Fe	Zn	Cr	Ni	Cd	Al	
589	(Starting Solution)	6.18	4.34	0.41	2.00	0.27	1.05	1.75
590	25 v/o	0.95	3.37	0.38	1.89	0.25	0.94	1.41
591	30 v/o	0.53	3.25	0.39	1.93	0.26	0.94	1.36
592	35 v/o	0.45	2.30	0.37	1.66	0.23	0.71	1.34
593	40 v/o	0.29	2.28	0.38	1.69	0.23	0.72	1.35
	(Controlled pH)							
594	25 v/o	0.82	2.07					
595	40 v/o	0.70	1.78					

NOTE:
- DEHPA mixed with Kermac 470B
- O/A = 1, 50cc each
- Temperature: 40°C
- 594, 595 controlled @ pH = 1.75

TABLE 8.36. SIMULATED CONTINUOUS LOAD/STRIP TEST USING 40% DEHPA ON COPPER FREE LEACH SOLUTION

Sample	Description	Concentration (gpl) after Organic Contact (or stripping contact)			
		Fe		Zn	
		gpl in Aqueous	gpl loaded in Organic	gpl in Aqueous	Gpl loaded in Organic
589	Starting Solution	6.18	----	4.34	----
612	E_{11}	.55	5.63	2.65	1.69
613	E_{12}	1.53	4.65	4.48	-.14
614	E_{13}	4.41	1.77	3.84	0.50
			12.05		2.05
615	S_{11}	0.42		1.53	
616	S_{12}	0.24		0.06	
617	S_{13}	0.30		0.03	
		.96 (8% stripped)		1.62 (79.0% stripped)	
618	E_{21}	4.77	1.41	2.72	1.62
619	E_{22}	4.78	1.40	3.92	0.42
620	E_{23}	5.29	0.89	4.74	-.40
			3.70		1.64
621	S_{21}	0.73		1.34	
622	S_{22}	0.53		0.20	
623	S_{23}	0.50		0.04	
		1.76 (12% of total stripped)		1.58 (76% of total stripped)	
624	E_{31}	3.54	2.64	3.90	0.44
625	E_{32}	4.31	1.87	4.05	0.29
626	E_{33}	4.16	2.02	3.80	0.54
			6.53		1.27

NOTE:
- 25 v/o DEHPA in 470B
- Temperature: 35-40°C
- pH (initial): 1.75 for loading from aqueous phase
- O/A = 1, 50 cc each
- Organic loaded via 3 contacts with fresh leach solution (E series)
- Organic stripped via 3 contacts with (A/O = 1) 300 gpl H_2SO_4 (S series)
- Three series of load and two series of strip tests conducted

probably with some Deconol, would be suitable, and even though there was no isotherm available, three stages of extraction seemed reasonable.

Up to this time, however, there had not been many stripping tests carried out, so this series of tests was an attempt to understand stripping behavior.

A simulated continuous cycling test was carried out by contacting one volume of 40% organic three times with Cu free 1.75 pH solution, the organic phase was then stripped two times with 300 gpl acid. Extraction was repeated, then the organic was stripped again, and finally loaded for the third time. The results are presented in Table 8.36. pH changes in the raffinates were essentially similar for each of the three contacts and the analytical data indicated fairly good extractions. However, only a few percent of the iron could be stripped.

8.3.3.5. Fe Extraction: Three-Stage Contacting

Copper free activated carbon treated (pH 1.75) raffinate was contacted three times with fresh 25 v/o (and a second test was made using 40 v/o) D_2EHPA organic. The pH change was measured on each raffinate.

The separations were quite rapid, and it was found that a small amount of muck formed but if it was separated after the first contact, no further muck developed.

Evidently most of the extractable iron (Fe^{+++}) was picked up in the first contact, with very little more occurring in the second and third stages. Zn on the other hand was progressively extracted; apparently Fe^{+3} loads first, then zinc is loaded. The results of these tests are presented in Table 8.37.

8.3.3.6. Fe Stripping

Each of the three organics from the 25% and 40% extractions were stripped with 40% H_2SO_4 (O/A = 10) in order to get some Fe^{+++} color into the strip solution. The phase separations were rapid and color did appear in the strip

TABLE 8.37. DEHPA EXTRACTION OF IRON AND ZINC: THREE STAGE CONTACTING

Sample	Description	Concentration in Solution (gpl) after Contact (O/A = 1) and Extraction from Solution (%)			
		Fe		Zn	
		gpl	% Ext.	gpl	% Ext.
657	Starting Solution , pH=2.2	5.64	----	3.85	----
	25 v/o DEHPA				
651	1st Contact	0.86	84.8	3.13	46.5
652	2nd Contact	0.64	25.6	1.87	40.2
653	3rd Contact	0.66	0	1.27	32.0
		Total Extracted	88.3%	Total Extracted	67.0%
	40 v/o DEHPA				
654	1st Contact	0.75	86.7	2.33	60.2
655	2nd Contact	0.65	13.3	1.18	49.4
656	3rd Contact	0.61	6.1	0.61	48.3
		Total Extracted	89.2%	Total Extracted	84.2%

NOTE: ·Copper free leach solution contacted three times with fresh organic.
·Temperature: 40°C, O/A = 1, 50 cc each phase.

from the first contact organic. Very little iron, but virtually all of the zinc was stripped; Table 8.38.

8.3.3.7. Fe Stripping: Variable Deconol Content

In previous work it had appeared that the presence of Deconol was deleterious to iron and zinc extraction but improved the stripping, so a series of tests were performed with various contents of Deconol in 25% D_2EHPA.

First the organic phase containing 5, 10, 15, and 20% Deconol was loaded by contacting with Cu free raffinate at 40^0C. Then the organic was stripped with 40% acid (O/A = 10).

These data agree with the previous results that Fe^{+3} stripping can be increased with Deconol but the degree of stripping is still poor; Table 8.39.

8.3.3.8. Reductive Stripping of Ferric Iron From D_2EHPA

Removal of ferric iron from D_2EHPA can be accomplished by use of hydrochloric acid. It can also be accomplished by reductive stripping. A number of experimental tests were performed to illustrate this fact, Tables 8.40 and 8.41 and 8.42.

If sulfuric acid is contacted with iron powder; the iron is filtered from the solution; then the solution is immediately contacted with the iron bearing organic phase, the ferric iron is stripped from the organic (Table 8.40). The disadvantage of the process is that iron is added to the strip solution. Similar tests were concluded using zinc (Table 8.41) and nickel (Table 8.42) rather than iron. Neither was very effective.

A study was also conducted to determine if ferrous iron was extracted from an aqueous solution by D_2EHPA (Table 8.43). Ferrous iron was not extracted. Strip tests using a reducing acid, i.e., sulfurous acid, were performed on ferric loaded D_2EHPA. Removal of ferric iron was unsuccessful (Table 8.44).

TABLE 8.38. DEHPA STRIPPING OF IRON AND ZINC (SEE TABLE 8.34 FOR LOADING DATA)

Sample	Condition	Concentration in Aqueous Strip (gpl) after One Contact (O/A = 10) and Extraction from Loaded Organic (%)			
		Fe		Zn	
		gpl	% Stripped	gpl	%Stripped
	25 v/o DEHPA				
658	Organic from 651 Stripped	0.29	1	6.45	89.6
659	Organic from 652 Stripped	0.029	1	9.23	73.3
660	Organic from 653 Stripped	Sample Lost		Sample Lost	
	40 v/o DEHPA				
661	Organic from 654 Stripped	0.14	0.5	12.5	82.2
662	Organic from 655 Stripped	0.017	2	6.93	60.2
663	Organic from 656 Stripped	0.012	3	3.51	61.4

NOTE: ·40% H_2SO_4 strip used. Each of the six organics from Table 8.37 stripped.
·Temperature: 40°C

TABLE 8.39. INFLUENCE OF DECONOL ON IRON STRIPPING FROM DEHPA

Sample	Condition	Concentration in Aqueous Strip (gpl) and Percent Stripped from Organic	
		Fe	
		gpl	% Stripped from Organic
657	Starting Solution	5.64	
	5 v/o Deconol		
664	Raffinate	1.69	
665	Strip	1.51	3.8
	10 v/o Deconol		
666	Raffinate	2.20	
667	Strip	2.37	6.8
	15 v/o Deconol		
668	Raffinate	1.14	
669	Strip	6.58	14.6
	20 v/o Deconol		
670	Raffinate	1.28	
671	Strip	6.75	15.5

NOTE:
- All tests used 25 v/o DEHPA, variable amounts of Deconol, remainder Kermac 470 B
- Temperature: 40°C
- Copper free leach solution contacted (O/A = 1); then organic stripped with 40% H_2SO_4 (O/A = 10)

TABLE 8.40. REDUCTIVE STRIPPING OF DEHPA. PRELIMINARY TESTS: IRON REDUCTANT

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Cr	Ni	Zn	Cd	Al
1336	Starting solution oxidized with H_2O_2, pH = 2.22	4.01	1.05	0.28	1.00	2.74	0.12	1.40
1338	Contacted (1336) 20 v/o DEHPA, 80 v/o KERMAC 470B, pH = 2.2, O/A = 1, 2 minutes, aqueous phase (pH = 1.04)	0.85	0.96	0.25	0.92	2.09	0.11	1.24
	Loaded organic phase	3.16	0.09	0.03	0.08	0.65	0.01	0.16
1339A	200 gpl H_2SO_4 contacted with iron powder 5 minutes, filtered	2.25	< D.L.	0.006	0.002	< D.L.	< D.L.	< D.L.
1339	1339A solution contacted with Fe loaded DEHPA	6.83	0.003	0.011	0.005	0.497	< D.L.	0.048
	Stripped (%) from DEHPA	100 (complete)				76		

Notes:
- 50 cc of oxidized leach solution contacted with 50 cc of 20 v/o DEHPA, O/A = 1, pH = 2.2
- Loaded organic (50 cc) contacted with 50 cc of 200 gpl H_2SO_4 which previously been contacted with iron powdwe. Contact with organic made immediately after iron-sulfuric acid contact.

TABLE 8.41. REDUCTIVE STRIPPING OF DEHPA: SULFURIC ACID CONTACTED WITH ZINC AND IRON

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Cr	Ni	Zn	Cd	Al
1424	Starting Organic; 20 v/o DEHPA, 80 v/o 470B; Contracted solution 1322, 40°C, O/A = 1, 2 min.	3.77	----	----	----	1.10	----	0.17
	Zinc Reactant							
1415	Solution 1424 contacted with 200 gpl H_2SO_4 (pre-treated with 1 gpl Zn then filtered: 0.16 gpl Zn dissolved)	0.05	----	----	----	0.70	----	0.004
1416	As above, except sulfuric acid solution pre-treated with 10 gpl Zn: 0.57 gpl Zn dissolved	0.02	----	----	----	1.09	----	0.006
	Strip Recovery (%)	(1415) 1%	----	----	----	56%	----	----
		(1416) 0.5%	---	----	----	66%	----	----
	Iron Reductant							
1417	Solution 1424 contacted with 200 gpl H_2SO_4 (pre-treated with 1 gpl Fe, then filtered: 0.33 gpl Fe dissolved	0.46	----	----	----	0.73	----	0.014

TABLE 8.41. CONTINUED

Sample No.	Condition	(concentration (gpl)						
		Fe	Cu	Cr	Ni	Zn	Cd	Al
1418	As above except sulfuric acid solution pretreated with 10 gpl Fe: 0.46 gpl Fe dissolved	4.07	----	----	----	0.60	----	0.009
	Strip Recovery (%)	(1417) 1% (1418) 96%	---- ----	---- ----	---- ----	66% 54%	---- ----	---- ----
	Sequence Test							
1419	Stripped loaded DEHPA with 200 gpl H_2SO_4 to remove zinc but not iron	0.04	----	----	----	0.57	----	0.015
1420	Retreat above organic with solution 1412 (10 gpl Zn pretreated solution)	0.07	----	----	----	0.55	----	0.008
	Strip Recovery (%)							
		3%	----	----	----	67%	----	----
1421	Stripped loaded DEHPA with 200 gpl H_2SO_4 to remove zinc but not iron	0.02	----	----	----	0.53	----	0.013

TABLE 8.41. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Cr	Ni	Zn	Cd	Al
1422	Retreat above organic with solution 1418 (10 gpl Fe pretreated solution)	4.37	----	----	----	0.02	----	0.010
	Strip Recovery (%)	100%	----	----	----	48%	----	----

NOTE: ·All contacts O/A = 1, R.T. 2 minutes, 50 cc of each solution.

·Eh values for reductive solutions given in following table.

TABLE B.42. REDUCTIVE STRIPPING OF DEHPA. PRELIMINARY TESTS: NICKEL REDUCTANT

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Cr	Ni	Zn	Cd	Al
1336	Starting Solution Oxidized with H_2O_2, pH = 2.22	4.01	1.05	0.28	1.00	2.74	0.12	1.40
1338	Contacted (1336) with 20 v/o DEHPA, 80 v/o 470B, pH = 2.2, O/A = 1, 2 minutes, aqueous phase pH = 1.04	0.85	0.96	0.25	0.92	2.09	0.11	1.24
	Loaded Organic Phase	3.16	0.09	0.03	0.08	0.65	0.01	0.16
1341A	200 gpl H_2SO_4 contacted with nickel powder, 5 minutes, filtered	0.009	< D.L.	0.006	0.068	<D.L.	<D.L.	< D.L.
1341	1341A solution contacted with Fe loaded DEHPA	0.77	0.008	0.006	0.059	0.43	< D.L.	0.080
	Stripped (%)	23.1				65.8		

Notes: . 50 cc of oxidized leach solution contacted with 50 cc of 20 v/o DEHPA, O/A = 1, pH = 2.2

. Loaded organic (50 cc) contacted with 50 cc of 200 gpl H_2SO_4 which previously been contacted with nickel powder. Contact with organic made immediately after nickel-sulfuric acid contact.

TABLE 8.43. DEHPA EXTRACTION OF ZINC FROM A ZN^{++}-FE^{++} SOLUTION

Sample	Condition	Concentration Remaining in Solution (gpl) and Extraction from Solution (%)				
		Fe^{++}			Zn^{++}	
		gpl		% Ext.	gpl	% Ext.
		Total Fe	Fe^{++}			
914	Starting Solution	12.00	11.9	----	9.00	----
918	Contacted with DEHPA at pH = 2	11.63	11.7	3.0	4.99	47.5
915	Starting Solution Adjusted to pH = 3.5	11.41		----	8.66	----
916	Contacted with DEHPA at pH = 3.5	10.78	10.5	5.5	3.86	55.4
919	Starting Solution Adjusted to pH = 4.0	10.80		----	8.19	----
920	Contacted with DEHPA at pH = 4.0	10.41	10.7	3.7	3.83	53.2

NOTE: ·25 v/o DEHPA, 10 v/o Deconol, 65 v/o Kermac 470B
·O/A = 2, 50 cc leach solution, 100 cc DEHPA solution
·Temperature: 40°C
·Phase separation good

TABLE 8.44 . STUDY ON THE POTENTIAL SULFUROUS ACID STRIPPING OF IRON FROM DEHPA

Sample	Condition	Concentration in Aqueous Phase (gpl)								
		Fe		Zn		Cu	Cr	Ni	Cd	Al
	Loading Organic O/A = 2	Aqueous	Organic	Aqueous	Organic					
905	Starting Leach Solution pH = 2	8.87	----	5.97	----	3.95	0.60	2.84	0.41	1.41
906	Contact 1, pH = 2.0	3.07	2.90	4.91	0.50	4.01	0.61	2.88	0.41	1.40
907	Contact 2, pH = 2.0	4.84	4.92	5.50	0.73	3.92	0.60	2.85	0.41	1.38
	Stripping Organic A/O = 2									
908	10 v/o Sulfurous Strip	0.018		0.185						
909	20 v/o Sulfurous Strip	0.018		0.220						
910	40 v/o Sulfurous Strip	0.016		0.295						
911	60 v/o Sulfurous Strip	0.016		0.323						
912	80 v/o Sulfurous Strip	0.016		0.359						
913	100 v/o Sulfurous Strip	0.016		0.332						

NOTE: ·Temperature: 40°C
·250 cc organic, 125 cc leach solution (Load)
·50 cc sulfurous acid solution, 25 cc loaded organic (Strip)

8.3.4. Iron Removal by Sludge Roasting

A few preliminary experiments were conducted to determine if iron could be rejected from the sludge by an acid bake-roast-dilute acid leach (based on Commercial L.R.E. process concept(39)), i.e., the concept is to convert the hydroxides to sulfates in an acid bake, then to preferentially convert the iron to an oxide form while leaving the other metal sulfates unoxidized. The sulfate in the resulting roasted product would be water or dilute acid soluble while iron would be insoluble. The results are presented in Tables 8.45-8.47. Further testwork was deemed unnecessary.

8.4. IRON AND ZINC REMOVAL (LOW IRON BEARING SLUDGES)

The experimental work described in Section 8.3.2. led to the conclusion that low iron bearing solutions could be effectively treated without the need for a jarosite precipitation unit operation. The major advantage of a flowsheet that eliminates jarosite precipitation is that chromium is not lost.

The differences in the low iron flowsheet and high iron flowsheet was presented previously in Figures 6.1 and 6.3. The major difference in the low iron flowsheet is that jarosite precipitation of iron is eliminated and iron is removed after solvent extraction of copper. Iron is removed by solvent extraction using D_2EHPA as the extractant. Iron is in fact removed separately in a continuous solvent extraction system in conjunction with the removal of zinc.

The experimental set-up is presented schematically in Figure 8.14. It consists of the following sequence of operations:

- Aqueous leach solution is pH adjusted to the range 1-1.2, then contacted with stripped organic (40 v/o D_2EHPA, 60 v/o KERMAC 510 kerosene). The aqueous solution at this point in the flowsheet contains iron, zinc, nickel and chromium. Iron (2-4 gpl) is extracted (to a few hundred ppm) from the aqueous phase into the organic phase by one stage of mixing. Some zinc is coextracted but chromium and nickel are unaffected.

- The iron loaded organic is transported to a second mixer where it is contacted with 200 gpl H_2SO_4. Zinc is stripped from the organic phase with the strip acid. Iron is unaffected.

TABLE 8.45. PRELIMINARY DESIGN MATRIX AND EXPERIMENTAL RESULTS FOR ACID PUG-SULFATION ROAST (1/2 REPLICA)

Sample		Sulfation Roast Time (Hrs.)	Sulfation Roast Temp. (°C)	Solution Leach Temp. (°C)	Acid Content of Leach		Cu	Fe	Cr	Ni	Zn	Cd
	Base	2	600	RT	0							
	Unit	1	200									
	High (+)	3	800	Boiling	5% H_2SO_4							
	Low (-)	1	400	RT	0							
	Test #						Cu	Fe	Cr	Ni	Zn	Cd
216	1	-	-	-	-		100.0	74.3	38.9	74.0	100.0	85.7
217	2	+	-	-	+		98.2	94.9	91.4	92.5	79.2	88.9
218	3	-	+	-	+		45.6	0.2	0.0	3.7	55.7	87.3
219	4	+	+	-	-		0.9	0.0	0.0	0.4	19.2	28.6
220	5	-	-	+	+		96.3	100.0	100.0	100.0	4.0	100.0
221	6	+	-	+	-		85.6	72.7	34.6	79.6	69.6	87.3
222	7	-	+	+	-		3.4	0.0	0.0	1.1	72.0	41.3
223	8	+	+	+	+		35.4	3.5	3.7	9.8	20.6	87.3
						Max. Exp. Variation						

Results - Extraction from Solid (%)

Effects	Average(%)				
Cu	58.2	-3.2	-36.8	-3.0	10.7
Fe	43.2	-0.4	-42.3	0.8	6.4
Cr	33.6	-1.1	-32.6	1.0	15.2
Ni	45.1	0.4	-41.4	2.5	6.4
Zn	52.5	-5.4	-10.7	-11.0	-12.7
Cd	75.8	-2.8	-14.7	3.2	15.2

NOTE:
- ·Starting Sludge A (23.4 ± 1.6% Solids)
- ·9.8 gm Conc. H_2SO_4/150 gm Sludge; pug roasted at 95°C for 3 hrs.
- ·Sulfation Roast in 4% O_2, 8% SO_2
- ·Solution Leach 30 Min., 10% Solids
- ·Solution Diluted to 500 cc for Analysis

TABLE 8.46. SULFATION AS A FUNCTION OF ROAST TEMPERATURE: EXTRACTION OF SOLID

Sample	Condition	Extraction from Solid (%)					
		Cu	Fe	Cr	Ni	Zn	Cd
957	No Roast	63.8	75.8	85.5	69.4	80.2	68.5
958	200°C	70.2	72.3	65.0	68.0	85.4	68.5
959	400°C	65.0	61.0	56.4	57.1	75.0	60.3
960	500°C	46.4	37.0	27.3	36.2	52.6	41.1
961	600°C	51.0	29.6	17.1	45.2	57.2	54.8
962	700°C	56.1	7.7	5.1	45.2	59.2	65.8

Notes:
- 10 g dry solid, barrel 2 sludge.
- Acid pugged with 10 cc H_2SO_4 @ 95°C for 3 hrs.
- Baked sample roasted at designated temperature in 4% O_2, 8% SO_2, 88% N_2 for one hour.
- Roasted sample leached in 1% H_2SO_4 for 30 minutes, filtered, washed, diluted to 500 cc (data corrected to leach solution volume of 200 cc)
- Starting solid composition: 18.29% Fe, 5.53% Ni, 2.80% Al, 1.17% Cr, 0.73% Cd, 11.47% Zn, 7.84% Cu, 1.05% Ca

TABLE 8.47. SULFATION AS A FUNCTION OF ROAST TEMPERATURE: DATA

Sample	Condition	Concentration in 200 cc Solution (gpl)						
		Cu	Fe	Cr	Ni	Zn	Cd	Al
957	No Roast	2.50	6.92	0.50	1.92	4.60	0.25	1.70
958	200°C	2.75	6.60	0.38	1.88	4.90	0.25	1.18
959	400°C	2.55	5.58	0.33	1.58	4.30	0.22	1.12
960	500°C	1.82	3.38	0.16	1.00	3.02	0.15	1.10
961	600°C	2.02	2.70	0.10	1.25	3.30	0.20	0.68
962	700°C	2.20	0.70	0.03	1.25	3.40	0.24	0.22

NOTE:
- 10 gm dry solid, Barrel #2
- Acid pugged with 10 cc H_2SO_4 @ 95°C for 3 hrs.
- Baked sample roasted at designated temperature in 4% O_2, 8% SO_2, 88% N_2 for one hour
- Roasted sample leached in 1% H_2SO_4 for 30 minutes, filtered, washed, diluted to 500ml (data corrected to leach solution volume of 200 cc
- Starting solid composition: 18.27% Fe, 5.53% Ni, 2.80% Al, 1.17% Cr, 0.73% Cd, 5.53% Ni, 11.47% Zn, 7.84% Cu, 1.05% Ca

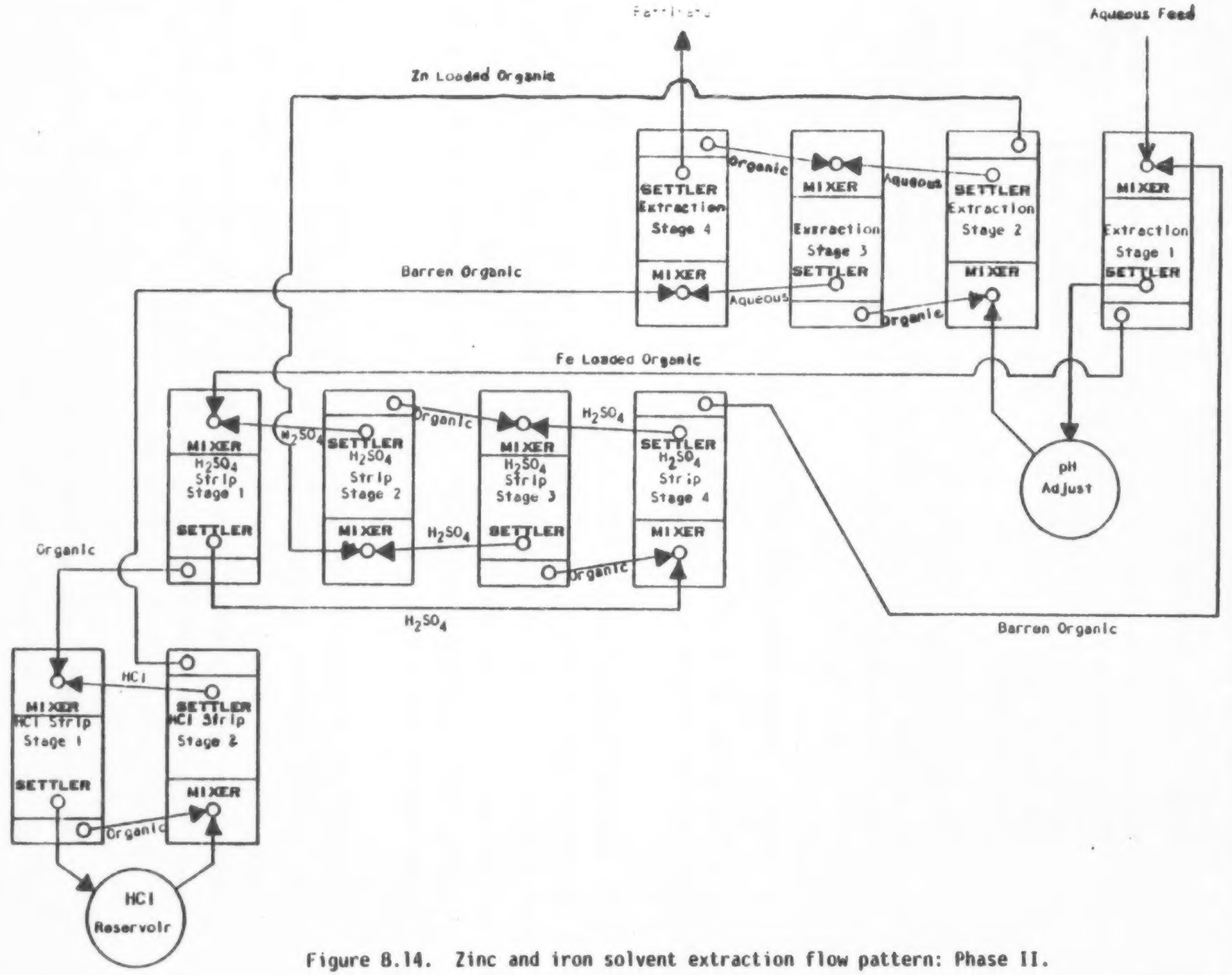

Raffinate
Aqueous Feed
Zn Loaded Organic
Barren Organic
Fe Loaded Organic
SETTLER
Extraction
Stage 4
MIXER
Organic
MIXER
Extraction
Stage 3
SETTLER
Aqueous
Aqueous
SETTLER
Extraction
Stage 2
MIXER
Organic
MIXER
Extraction
Stage 1
SETTLER
pH
Adjust
MIXER
H_2SO_4
Strip
Stage 1
SETTLER
H_2SO_4
SETTLER
H_2SO_4
Strip
Stage 2
MIXER
Organic
MIXER
H_2SO_4
Strip
Stage 3
SETTLER
H_2SO_4
H_2SO_4
SETTLER
H_2SO_4
Strip
Stage 4
MIXER
Organic
H_2SO_4
Barren Organic
Organic
HCl
MIXER
HCl Strip
Stage 1
SETTLER
SETTLER
HCl Strip
Stage 2
MIXER
Organic
HCl
Reservoir

Figure 8.14. Zinc and iron solvent extraction flow pattern: Phase II.

- The iron loaded organic is transported to a third, fourth and fifth mixer where it is contacted with 6 N HCl. Iron is stripped from the organic phase into the strip acid.

- The iron, zinc depleted organic phase, is transported to a series of three mixers where it is contacted with the iron depleted aqueous leach solution. The aqueous phase pH is raised to 2.0. Zinc is extracted from the aqueous phase into the organic phase. Chromium and nickel were unaffected. The raffinate is relatively free of zinc (<50 ppm).

- The zinc loaded organic phase is transported to two mixers where it is contacted with 200 gpl H_2SO_4. Zinc is stripped from the organic phase into the strip acid. The organic is recycled back to the first mixer to contact fresh leach solution containing iron and zinc.

8.4.1. Large Scale Iron and Zinc Removal

The results of a series of studies using the Reister one-gallon mixer-settler solvent extraction rack are presented in Tables 8.48-8.49.

Earlier testwork showed that a muck problem resulted in the first extraction cell if the iron content was in the range of a few grams per liter at a pH of about two. Follow-up testwork showed that the muck problem was minimized by lowering the feed leach solution pH (decreased iron and zinc loading into the organic phase) and by changing the kerosene diluent (from KERMAC 470 to 510, a low aromatic solvent).

A series of coextraction tests were conducted using the solvent extraction flow pattern depicted schematically in Figure 8.15. The results of two large scale tests are presented in Table 8.48. The test results showed that coextraction of iron and zinc was excellent and controllable and that muck formation was minimized by running the first stage organic continuous instead of aqueous continuous.

The above tests were followed by continuous large scale testwork over a four day period. Sludge was leached, copper was extracted by LIX 622 extraction and the resulting solution was used for the four day test run. A total of 365 liters of aqueous leach solution was exposed to 38.8 liters of organic phase (Table 8.49). No degradation of the organic phase was noted.

TABLE 8.48. LARGE SCALE IRON-ZINC EXTRACTION TESTWORK (PHASE II, LOW IRON PRELIMINARY TESTWORK)

Sample No.	Conditions	Concentration in Aqueous, gpl							Extraction Efficiency, %	
		Fe	Cu	Zn	Cr	Ni	Al	Ca	Zn	Fe
	Large Scale Test on co-extraction of Fe & Zn where pH control exercised in 1st and 2nd cells (see notes below)									
	Starting solution, 75 l									
3208	1st Cell Feed, pH = 0.62	1.728	----	2.425	6.471	2.502	0.029	0.702		
3216	2nd Cell Feed, pH = 1.56	1.165	----	2.164	5.959	2.319	0.027	----	10.8	32.6
3217	4th Cell Final Raffinate 5 hrs. continuous test	0.011	----	0.048	6.153	2.829	0.014	---	98.0	99.0
	Large Scale Test on co-extraction of Fe & Zn where pH control exercised in 1st and 2nd Cells and the 1st Cell was run organic continuous									
3255	First Cell Feed, pH = 0.95 Temp. = 22^{0}C	1.611	---	2.231	5.470	2.547	0.035	0.696		
	1 Hr.									
3250	1st Cell Raffinate, pH = 0.83, 22^{0}C	0.7475	----	1.935	5.664	2.602	0.036	0.652	13.3	53.6
3251	2nd Cell Feed, pH = 2.03, 25^{0}C	0.764	----	2.121	5.031	2.077	0.040	0.635		

TABLE 8.48. CONTINUED

Sample No.	Conditions	Concentration in Aqueous, gpl							Extraction Efficiency, %	
		Fe	Cu	Zn	Cr	Ni	Al	Ca	Zn	Fe
3252	4th Cell Raffinate, pH = 1.15, 21°C	0.009	----	0.067	5.010	1.870	0.005	0.220	96.8	98.8
	3 Hrs.									
3256	1st Cell Raffinate, pH = 0.89, 37°C	0.373	----	1.586	5.659	2.587	0.032	0.692	28.9	76.8
3257	2nd Cell Feed, pH = 1.91, 58°C	0.482	----	1.685	5.394	2.448	0.026	0.661		
3258	4th Cell Raffinate, pH = 1.34, 28°C	0.020	----	0.022	5.589	2.392	6.005	0.322	98.6	95.9
	5 Hrs. (end of run)									
3261	1st Cell Raffinate, pH = 0.88, 30°	0.430	----	1.754	5.614	2.558	0.034	0.722	21.4	73.3
3262	2nd Cell Feed, pH = 1.80, 58°	0.385	----	1.676	5.292	2.430	0.031	0.707		
3263	4th Cell Raffinate, pH = 1.19, 25°C	0.018	----	0.046	4.981	2.149	0.012	0.317	97.2	95.3

NOTES:

- System set-up described in Section 8.4.1.
- Conditions of first large scale test: 75 liters of leach solution, 38.8 liters 40% DEHPA in 470-B, 18.2 liters of 200 gpl H_2SO_4, 27 liters 4N HCl, flowrate = 0.25 l/min., total exposure time = 5 hrs.
- Comments on first large scale test: Some crud noticeable in Cell #2 1/2 hour after run began, but formation remained minimal for this experiment. Run demonstrated that crud formation can be controlled by pH manipulation and still achieve satisfactory extraction of 3.5 g/l combined Fe and Zn. Iron was not stripped very well in this run.
- Conditions of second large scale test: 75 liters of leach solution, 38.8 liters 40 v/o DEHPA in 470-B, 18.2 liters H_2SO_4, 27 liters 4.5N HCl, flowrate = 25 liters/min., total exposure = 5 hrs.
- Comments on second large scale coextraction test: organic continuous operation in 1st Cell mixer exhibited positive results on minimizing crud formation for this mode of mixer operation.

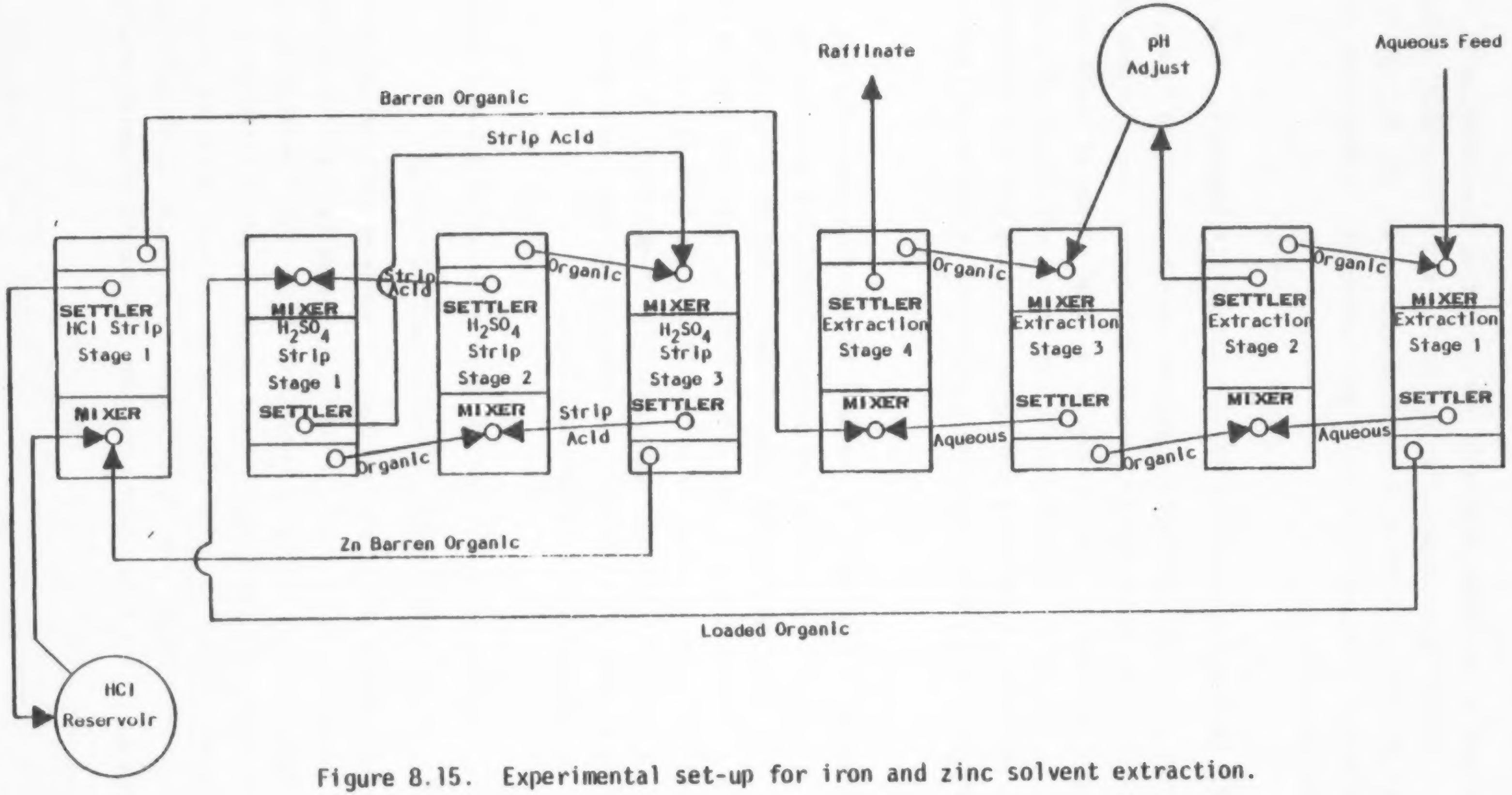

Raffinate
pH Adjust
Aqueous Feed
Barren Organic
Strip Acid
SETTLER HCl Strip Stage 1
MIXER
MIXER H_2SO_4 Strip Stage 1
SETTLER
Strip Acid
SETTLER H_2SO_4 Strip Stage 2
MIXER
Organic
MIXER H_2SO_4 Strip Stage 3
SETTLER
Strip Acid
Organic
SETTLER Extraction Stage 4
MIXER
Organic
MIXER Extraction Stage 3
SETTLER
Aqueous
SETTLER Extraction Stage 2
MIXER
Organic
Organic
MIXER Extraction Stage 1
SETTLER
Aqueous
Zn Barren Organic
Loaded Organic
HCl Reservoir

Figure 8.15. Experimental set-up for iron and zinc solvent extraction.

Cell efficiencies for iron, zinc and iron plus zinc are reported in Tables 8.50-8.52. Overall extraction efficiencies for end of run (EOR) solutions showed: 97.4% iron extraction; 97.3% zinc extraction; and 95.1-99.2% iron plus zinc extraction. Final solution raffinate contained: 0.053-0.095 gpl iron and 0.040-0.061 gpl zinc.

8.4.2. Continuous Long Term Solvent Extraction Testwork: Iron and Zinc

A series of solvent extraction studies were conducted to investigate: iron and zinc extraction stage and process efficiency; and possible degradation of the organic extractant when exposed to a large volume of leach solution, i.e., what is the effect on the organic extraction efficiency of a large number of load/strip cycles. A schematic diagram depicting the flow patterns in the test system for the aqueous and organic solutions is presented later in Figure 8.20.

The tests were conducted in the Bell Engineering testrack; 7.6 liters of 40 volume percent D_2EHPA - 85 volume percent KERMAC 510 kerosene was contacted with 150 liters of aqueous leach solution over a period of 67 hours. Approximately 58 load/strip cycles were achieved. Over 232 loading contacts and over 586 stripping contacts were made during the test period. An aqueous/organic contact ratio of approximately 20 was achieved. The results of the study are summarized in Table 8.53; stage efficiency and process rack efficiency are summarized in Tables 8.55-8.57.

8.4.3. Crud Formation and Control During Iron-Zinc Solvent Extraction

8.4.3.1. Crud Formation in D_2EHPA Solvent Extraction

A problem developed during the Phase II large scale iron and zinc solvent extraction testwork, i.e., crud formed in the first cell of the extraction (loading) stage and was initially uncontrollable. The flowsheet being tested during that period was two stages of extraction at pH 2 followed by readjusting the pH back to 2-2.5 after the second cell prior to entry into extraction cells 3 and 4. The formation of crud in the first cell created several problems. The first cell interface was uncontrollable; crud was

TABLE 8.49. LARGE SCALE IRON-ZINC EXTRACTION TESTWORK: LOW IRON FLOWSHEET, FOUR DAY CONTINUOUS TEST

Sample	Conditions	Concentration, gpl								
		Fe	Cu	Zn	Cr	Ni	Al	Ca	pH	T, ^{o}C
	First Day									
3282-B	1st Cell Feed, 75 l	1.164	0.069	1.815	5.749	5.340	0.041	0.602	1.58	76
	3 Hrs.									
3282-B	1st Cell Raffinate	0.137	0.126	1.347	5.589	5.318	0.038	0.608	1.15	134
3283-B	2nd Cell Feed	0.187	0.088	1.398	5.540	4.806	0.024	0.636		
	5 Hrs. (end of run)									
3284	4th Cell Raffinate	----	0.040	0.014	5.808	3.789	0.009	0.408	1.39	36
	Second Day									
3311	1st Cell Feed, 75 l	1.532	0.308	2.208	4.395	11.511	0.040	0.246	1.19	30
	1 Hr.									
3312	1st Cell Raffinate	0.265	0.281	1.479	4.066	10.717	0.041	0.229	1.05	30
3313	2nd Cell Feed	0.207	0.210	1.087	4.957	8.645	0.025	0.252	1.64	50
3314	4th Cell Raffinate	----	0.105	0.032	5.572	6.298	----	1.015	1.50	30
	3 Hrs.									
3319	1st Cell Raffinate	0.237	0.423	1.433	3.886	13.531	0.044	0.158	----	
3320	2nd Cell Feed	0.227	0.308	1.287	4.213	11.011	0.038	0.209	1.96	59
3321	4th Cell Raffinate	0.008	0.210	0.054	4.591	9.739	----	0.026	1.28	30
	5 Hrs. (end of run)									
3326	1st Cell Raffinate	0.249	0.414	1.304	3.688	12.641	0.049	0.151	----	
3327	2nd Cell Feed	0.279	0.380	1.342	4.031	12.448	0.057	0.219	----	

TABLE 8.49. CONTINUED

Sample	Conditions	Concentration, gpl								
		Fe	Cu	Zn	Cr	Ni	Al	Ca	pH	T, °C
3328	4th Cell Raffinate	0.040	0.284	0.028	4.212	11.570	0.018	0.045	----	----
3331	4th Cell Composite Raffinate	0.065	0.182	0.040	4.927	8.443	0.011	0.057	----	----
	Third Day									
3351	1st Cell Feed, 75 l	1.891	0.563	2.220	4.931	11.650	0.071	0.372	1.27	23
	1 Hr.									
3353	1st Cell Raffinate	0.377	0.567	1.499	4.844	12.030	0.054	0.288	1.11	25
3354	2nd Cell Feed	0.251	0.456	1.427	4.278	12.370	0.058	0.242	2.11	54
3355	4th Cell Raffinate	0.020	0.341	0.040	4.110	11.996	0.010	0.024	1.37	30
	3 Hrs.									
3357	1st Cell Raffinate	0.368	0.573	1.441	4.967	12.140	0.061	0.302	1.08	25
3358	2nd Cell Feed	0.317	0.521	1.426	4.737	12.196	0.056	0.288	2.35	50
3359	4th Cell Raffinate	0.008	0.440	0.028	4.550	12.406	0.008	0.052	1.38	35
	5 Hrs.									
3363	1st Cell Raffinate	0.430	0.622	1.787	5.473	13.214	0.069	0.302	1.05	25
3368	2nd Cell Feed	0.351	0.534	1.558	4.939	11.972	0.061	0.305	1.94	41
3364	2nd Cell Raffinate	0.056	0.594	0.234	5.392	13.361	0.025	0.199	1.53	30
3365	3rd Cell Raffinate	0.026	0.608	0.082	5.379	13.415	0.023	0.106	1.22	26
3366	4th Cell Raffinate	0.024	0.551	0.060	5.132	12.996	0.019	0.062	----	----
3367	4th Cell Composite	0.010	0.391	0.043	4.599	12.011	0.002	0.046	1.26	24
	Fourth Day									
3414	1st Cell Feed, 140 l	2.362	0.370	2.436	4.258	8.527	0.057	0.441	1.39	23

TABLE 6.49. CONTINUED

Sample	Conditions	Fe	Cu	Zn	Cr	Ni	Al	Ca	pH	T, °C
		Concentration, gpl								
	1 Hr.									
3416	1st Cell Raffinate	0.475	0.363	1.604	4.181	8.593	0.0522	0.3119	1.20	25
3421	2nd Cell Feed	0.459	0.513	1.605	4.938	11.348	0.0575	0.3044	1.76	40
3417	2nd Cell Raffinate	0.107	0.538	0.304	5.072	12.102	0.0217	0.2711	1.57	35
3418	3rd Cell Raffinate	0.045	0.599	0.112	5.107	12.544	0.0160	0.1503	1.49	29
3419	4th Cell Raffinate	0.025	0.531	0.073	5.051	12.536	0.0153	0.0859	1.32	26
	3 Hrs.									
3422	1st Cell Raffinate	0.467	0.367	1.543	4.237	8.709	0.0507	0.3035	1.20	27
3427	2nd Cell Feed	0.458	0.423	1.666	4.698	9.880	0.0495	0.3051	1.88	48
3423	2nd Cell Raffinate	0.070	0.418	0.154	4.404	9.619	0.0123	0.2402	1.67	43
3424	3rd Cell Raffinate	0.034	0.434	0.066	4.430	9.824	0.0063	0.1606	1.56	38
3425	4th Cell Raffinate	0.024	0.423	0.044	4.406	9.915	0.0099	0.1197	1.27	34
	5 Hrs.									
3428	1st Cell Raffinate	6.429	0.373	1.684	4.426	9.229	0.0490	0.3274	1.22	29
3433	2nd Cell Feed	0.426	0.402	1.638	4.617	9.480	0.0546	0.3252	1.73	42
3429	2nd Cell Raffinate	0.084	0.391	0.229	4.477	9.420	0.0144	0.2865	1.59	41
3430	3rd Cell Raffinate	0.068	0.409	0.080	4.441	9.405	0.0066	0.2320	1.48	36
3431	4th Cell Raffinate	0.064	0.395	0.060	4.428	9.428	0.0073	0.1822	1.27	33
	7 Hrs.									
3437	1st Cell Raffinate	0.446	0.379	1.498	4.439	8.795	0.0526	0.3224	1.21	29
3442	2nd Cell Feed	0.526	0.383	1.723	4.264	8.822	0.0538	0.3306	1.95	48
3438	2nd Cell Raffinate	0.132	0.365	0.194	4.243	8.574	0.0152	0.2993	1.64	45
3439	3rd Cell Raffinate	0.053	0.400	0.079	4.356	8.713	0.0095	0.2811	1.54	41
3440	4th Cell Raffinate	0.047	0.358	0.050	4.360	8.659	0.0056	0.1911	1.31	36

TABLE 8.49. CONTINUED

Sample	Conditions	Concentration, gpl								
		Fe	Cu	Zn	Cr	Ni	Al	Ca	pH	T, °C
	9 Hrs. (end of run)									
3444	1st Cell Raffinate	0.403	0.352	1.694	4.265	8.544	0.0461	0.3225	1.21	31
3453	2nd Cell Feed	0.484	0.371	1.644	4.231	8.563	0.0519	0.3328	1.91	43
3445	2nd Cell Raffinate	0.110	0.353	0.186	4.296	8.504	0.0161	0.2992	1.67	44
3446	3rd Cell Raffinate	0.051	0.386	0.068	4.192	8.647	0.0086	0.2542	1.53	38
3447	4th Cell Raffinate	0.052	0.368	0.053	4.286	8.826	0.0080	0.1936	1.28	35
3454	End of run Composite Raffinate	0.053	0.369	0.061	4.469	9.181	0.0089	0.1633	1.29	31

NOTES: ·Leach: All leaches performed under standard conditions, 12,000 g sludge, 1650 cc concentrated H_2SO_4, 417 g $ZnSO_4 \cdot H_2O$, 886 g $CuSO_4 \cdot 5H_2O$, 300 cc H_2O_2 (30%), diluted to 75.0 liters with deionized water.

·Conditions: 38.8 liters 40 v/o DEHPA, 60 v/o KERMAC 470-B; 27 liters 4.7 N HCl; 18.2 liters 200 gpl H_2SO_4, 0.25 liters/min. feed, Cell #1 maintained organic continuous with recycle of 0.1 liters/min. organic from settler back to mixer.

TABLE 8.50. CELL EFFICIENCY FOR IRON EXTRACTION BY DEHPA: LARGE SCALE CONTINUOUS TESTWORK

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
	First Day, 75 l									
3281-B 3283-B	First Cell Feed, 1.164 gpl Fe Second Cell Feed, 0.187 gpl Fe									
3284	5 Hrs. (E.O.R.)	----	----	----	----	----	----	0.014	----	98.8
	Second Day, 71 l									
3311 3327	First Cell Feed, 1.532 gpl Fe Second Cell Feed, 0.279 gpl Fe									
3326,28	5 Hrs. (E.O.R)	0.249	83.7	----	----	----	----	0.040	----	97.4
3331	Final Composite Raffinate: 0.065 gpl Fe									
	Third Day, 75 l									
3351 3368	First Cell Feed, 1.891 gpl Fe Second Cell Feed, 0.351 gpl Fe									
3363,64 65,66	5 Hrs. (E.O.R.)	0.430	77.3	0.056	84.0	0.026	53.6	0.024	7.7	98.7
3370	Final Composite Raffinate: 0.095 gpl Fe									
	Fourth Day, 75 l									
3414	First Cell Feed, 2.362 gpl Fe									

TABLE 8.50. CONTINUED

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
3416,17 18,19	1 Hr.	0.475	79.9	0.107	76.7	0.045	57.9	0.025	44.4	98.9
3421	Second Cell Feed, 0.45 gpl Fe									
3422,23 24,25	3 Hrs.	0.467	80.2	0.070	84.7	0.034	51.4	0.024	29.4	99.0
3427	Second Cell Feed, 0.458 gpl Fe									
3428,29 30,31	5 Hrs.	0.429	81.8	0.084	80.6	0.068	19.0	0.064	6.2	97.3
3433	Second Cell Feed, 0.432 gpl Fe									
3437,38 39,40	7 Hrs.	0.446	81.1	0.132	74.9	0.053	59.8	0.047	11.3	98.0
3442	Second Cell Feed, 0.526 gpl Fe									
3444,45 46,47	9 Hrs. (E.O.R.)	0.403	82.9	0.110	77.3	0.051	53.6	0.052	----	97.7
3453	Second Cell Feed, 0.484 gpl Fe									
3454	Final Raffinate: 0.053 gpl Fe									

NOTES: 'Detailed data presented in Table 8.49.
'Cell efficiency decreases from cell to cell because pH of the leach solution drops off.

TABLE 8.51. CELL EFFICIENCY FOR ZINC EXTRACTION BY DEHPA: LARGE SCALE CONTINUOUS TESTWORK

Sample No.	Conditions	Stage Efficiency, gpl in Raffinate, % Extracted								
		Cell 1		Cell 2		Cell 3		Cell 4		Total Efficiency
		gpl	%	gpl	%	gpl	%	gpl	%	
	First Day, 75 l									
3281-B 3283-B	First Cell Feed, 1.815 gpl Zn Second Cell Feed, 2.398 gpl Zn									
3284	Five Hours (E.O.R.)	----	----	----	----	----	----	0.014	----	99.2
	Second Day, 75 l									
3311 3327	First Cell Feed, 2.208 gpl Zn Second Cell Feed, 1.342 gpl Zn									
3326, 28 3331	Five Hours (E.O.R.) Final Composite Raffinate: 0.040 gpl Zn	1.304	40.9	----	----	----	----	0.028	----	98.7
	Third Day, 75 l									
3351 3368	First Cell Feed, 2.220 gpl Zn Second Cell Feed, 1.558 gpl Zn									
3363, 64, 65, 66	Five Hrs. (E.O.R.)	1.787	19.5	0.234	87.0	0.082	64.5	0.060	26.8	97.3
3370	Final Composite Raffinate: 0.043 gpl Zn									
	Fourth Day, 140 l									
3414	First Cell Feed, 2.436 gpl Zn									
3416, 17, 18, 19	1 Hr.	1.604	34.2	0.304	81.0	0.112	63.2	0.073	34.8	97.0

TABLE 8.51. CONTINUED

Sample No.	Conditions	Stage Efficiency, gpl in Raffinate, % Extracted								
		Cell 1		Cell 2		Cell 3		Cell 4		Total Efficiency
		gpl	%	gpl	%	gpl	%	gpl	%	
3421	Second Cell Feed, 1.605 gpl Zn									
3422, 23, 24, 25	3 Hrs.	1.543	36.7	0.154	90.7	0.066	57.1	0.044	33.3	98.2
3427	Second Cell Feed, 1.666 gpl Zn									
3428, 29, 30, 31	5 Hrs.	1.684	30.9	0.229	86.0	8.080	65.1	0.060	25.0	97.5
3433	Second Cell Feed, 1.638 gpl Zn									
3437, 38, 39, 40	7 Hrs.	1.498	38.5	0.194	88.7	0.079	59.3	0.050	36.7	97.9
3442	Second Cell Feed, 1.723 gpl Zn									
3444, 45, 46, 47	9 Hrs. (E.O.R.)	1.694	30.5	0.186	88.7	0.068	63.4	0.053	23.9	97.8
3453	Second Cell Feed, 1.644 gpl Zn									
3454	Final Composite Raffinate: 0.061 gpl Zn									

NOTES: 'Detailed data presented in Table 8.49.
'Cell efficiency decreases from cell to cell because pH of the cell feed drops off.

TABLE 8.52. CELL EFFICIENCY FOR ZINC PLUS IRON EXTRACTION BY DEHPA: LARGE SCALE CONTINUOUS TESTWORK

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
	First Day, 75 l									
	5 Hrs. (E.O.R.)	----	----	----	----	----	----	0.014	----	99.2
	Second Day, 75 l									
	5 Hrs. (E.O.R.)	2.553	30.5	----	----	----	----	0.068	----	97.0
	Third Day, 75 l									
	5 Hrs. (E.O.R.)	2.217	46.1	0.290	84.8	0.108	62.8	0.084	22.2	98.0
	Final Composite Raffinate: 0.138 gpl (Fe + Zn)									
	Fourth Day, 140 l									
	9 Hrs. (E.O.R.)	2.097	56.3	0.296	86.1	0.119	60.0	0.105	11.8	95.1
	Final Composite Raffinate: 0.111 gpl (Fe + Zn)									

NOTES: 'Detailed data presented in Table 8.49.
'Cell efficiency decreases from cell to cell because pH of the leach solution drops off.

TABLE 8.53. CONTINUOUS DEHPA TESTWORK DATA SUMMARY: BELL SYSTEM

Sample No.	Conditions, End of Run Results	Concentration in Final Composite Raffinate, gpl						
		Fe	Cu	Zn	Cr	Ni	Al	Ca
	First Day, 19 1, 14 hrs.							
3745	First Stage Feed	2.023	0.015	1.828	4.620	7.773	0.033	0.206
3786	Second Stage Feed	1.245	0.017	1.058	4.727	7.986	0.030	0.147
	Loading							
3795	1st Cell Raffinate	0.925	0.011	1.207	4.702	7.853	0.024	0.172
3796	2nd Cell Raffinate	0.423	0.010	0.117	4.632	7.705	---	0.030
3797	3rd Cell Raffinate	0.409	0.018	0.043	4.808	8.235	---	0.009
3798	4th Cell Raffinate	0.342	0.005	0.017	4.724	8.124	0.002	0.004
3787	Composite Raffinate	0.498	0.008	0.080	4.679	7.990	0.003	0.015
	Stripping							
3799	5th Cell, H_2SO_4	0.077	---	39.35	0.235	0.283	0.045	0.514
3800	6th Cell, "	0.075	0.006	39.06	0.174	0.223	0.037	0.416
3801	7th Cell, "	0.063	---	38.50	0.167	0.222	0.033	0.415
3802	8th Cell, HCl	3.354	0.017	0.403	0.065	0.101	0.014	0.005
3803	9th Cell, "	3.496	---	0.396	0.073	0.053	0.025	0.005
3804	10th Cell, "	4.046	0.002	0.451	0.083	0.070	0.006	0.028
	Second Day, 19 1, 9 hrs.							
3805	1st Stage Feed	2.276	0.005	0.354	5.471	8.298	0.013	0.049
3806	2nd Stage Feed	1.364	0.015	0.987	5.088	8.585	0.044	0.147
	Loading							
3824	1st Cell Raffinate	0.515	0.023	0.329	5.434	8.234	0.010	0.046
3825	2nd Cell Raffinate	0.234	0.021	0.528	5.187	8.690	0.031	0.153
3826	3rd Cell Raffinate	0.146	0.019	0.315	5.072	8.629	0.026	0.135

TABLE 8.53. CONTINUED

Sample No.	Conditions, End of Run Results	Concentration in Final Composite Raffinate, gpl						
		Fe	Cu	Zn	Cr	Ni	Al	Ca
3827	4th Cell Raffinate	0.109	0.031	0.192	5.044	8.478	0.020	0.103
3835	Composite Raffinate	0.070	0.033	0.094	4.805	8.212	0.004	0.020
	Stripping							
3828	5th Cell, H_2SO_4	0.076	0.009	32.55	0.230	0.269	0.080	0.578
3829	6th Cell, "	0.061	0.019	30.23	0.225	0.247	0.070	0.491
3830	7th Cell, "	0.070	0.022	31.89	0.221	0.257	0.061	0.473
3831	8th Cell, HCl	2.885	0.017	0.140	0.027	0.018	0.017	0.004
3832	9th Cell, "	3.368	0.007	0.139	0.012	0.018	0.021	0.003
3833	10th Cell, "	5.533	0.009	0.250	0.012	0.023	0.023	0.004
	Third Day, 19 1, 6.5 hrs.							
3846	1st Stage Feed	2.742	0.010	2.207	5.487	7.872	0.045	0.052
3847	2nd Stage Feed	0.485	0.007	0.299	5.139	7.499	0.012	0.045
	Loading							
3860	1st Cell Raffinate	0.854	0.024	0.975	5.803	8.480	0.026	0.032
3861	2nd Cell Raffinate	0.055	0.007	0.043	5.494	8.402	0.004	0.008
3862	3rd Cell Raffinate	0.018	0.026	0.039	5.424	8.347	0.002	0.003
3863	4th Cell Raffinate	0.027	0.012	0.035	5.551	8.548	0.003	0.002
3871	Composite Raffinate	0.030	0.017	0.106	5.287	8.188	0.009	0.040
	Stripping							
3864	5th Cell, H_2SO_4	0.042	0.024	34.25	0.812	0.530	0.097	0.632
3865	6th Cell, "	0.056	0.019	34.31	0.662	0.464	0.096	0.674
3866	7th Cell, "	0.043	0.026	34.47	0.665	0.458	0.093	0.624
3867	8th Cell, HCl	2.868	0.004	0.147	0.001	0.015	0.016	0.009
3868	9th Cell, "	3.121	0.009	0.138	0.001	0.019	0.019	0.008
3869	10th Cell, "	3.870	0.002	0.237	0.014	0.030	0.022	0.011

TABLE 8.53. CONTINUED

Sample No.	Conditions, End of Run Results	Concentration in Final Composite Raffinate, gpl							
		Fe	Cu	Zn	Cr	Ni	Al	Ca	
	Fourth Day, 19 1, 8 hrs.								
3881	1st Stage Feed	2.035	0.099	2.128	5.304	7.550	0.007	0.015	
3882	2nd Stage Feed	1.311	0.016	1.501	5.013	7.269	0.048	0.042	
	Loading								
3895	1st Cell Raffinate	0.138	0.004	1.427	5.625	7.642	0.009	0.015	---
3896	2nd Cell Raffinate	0.772	0.019	1.270	5.026	7.364	0.025	0.015	---
3897	3rd Cell Raffinate	0.586	0.028	0.082	5.005	7.259	0.012	0.008	---
3898	4th Cell Raffinate	0.513	0.023	0.038	4.829	7.253	0.008	0.004	---
3908	Composite Raffinate	0.319	0.017	0.046	4.839	7.292:	---	0.004	---
	Stripping								
3899	5th Cell, H_2SO_4	0.057	0.028	38.83	0.948	0.649	0.1610	0.8871	---
3900	6th Cell, "	0.069	0.022	37.27	0.869	0.580	0.1546	0.7150	---
3901	7th Cell, "	0.077	0.014	37.19	0.904	0.605	0.1446	0.8046	---
3902	8th Cell, HCl	3.039	---	0.203	0.001	0.005	0.0163	0.0100	---
3903	9th Cell, "	3.352	---	0.182	---	0.004	0.0241	0.0133	---
3904	10th Cell, "	5.191	---	0.359	0.004	0.013	0.0267	0.0157	---
	Fifth Day, 19 1, 6.5 hrs.								
3926	1st Stage Feed	2.218	---	1.999	5.012	6.615	0.054	0.003	0.055
3927	2nd Stage Feed	0.509	---	1.636	5.613	7.867	0.005	0.015	0.070
	Loading								
3933	1st Cell Raffinate	1.119	0.006	1.921	5.223	6.962	0.058	0.004	---
3934	2nd Cell Raffinate	0.114	0.016	0.440	5.600	8.005	0.008	0.009	---
3935	3rd Cell Raffinate	0.065	0.013	0.129	5.729	7.956	0.008	0.005	---

TABLE 8.53. CONTINUED

Sample No.	Conditions, End of Run Results	Concentration in Final Composite Raffinate, gpl							
		Fe	Cu	Zn	Cr	Ni	Al	Ca	
3936	4th Cell Raffinate	0.056	0.006	0.075	5.740	7.996	0.003	0.003	
3944	Composite Raffinate	0.022	---	0.031	5.127	7.398	0.006	0.002	---
	Stripping								
3937	5th Cell, H_2SO_4	0.050	0.015	33.85	0.766	0.532	0.153	0.6141	---
3938	6th Cell, "	0.067	0.007	32.11	0.769	0.530	0.151	0.498	---
3939	7th Cell, "	0.069	---	32.06	0.749	0.514	0.142	0.508	---
3940	8th Cell, HCl	2.293	---	0.159	---	0.010	0.013	0.010	---
3941	9th Cell, "	2.506	---	0.184	---	0.004	0.019	0.010	---
3942	10th Cell, "	3.630	---	0.274	---	0.004	0.020	0.010	
	Sixth Day, 19 1, 6.5 hrs.								
3953	1st Stage Feed	2.127	0.020	2.162	5.712	7.124	0.010	0.003	0.628
3954	2nd Stage Feed	1.005	0.020	1.617	4.604	6.100	0.060	0.004	---
	Loading								
3972	1st Cell Raffinate	0.388	0.027	1.527	4.965	6.354	0.009	0.005	0.530
3973	2nd Cell Raffinate	0.453	0.024	0.383	4.348	5.819	0.038	0.002	0.471
3974	3rd Cell Raffinate	---	0.028	0.108	---	6.092	0.021	0.0016	0.521
3975	4th Cell Raffinate	0.238	0.026	0.046	3.466	4.774	0.011	0.0084	0.381
3969	Composite Raffinate	0.238	0.022	0.050	5.335	6.763	0.012	0.0072	0.517
	Stripping								
3976	5th Cell, H_2SO_4	0.077	0.018	---	0.769	0.548	0.206	0.437	0.451
3977	6th Cell, "	0.083	0.020	---	0.666	0.487	0.168	0.389	0.357
3978	7th Cell, "	0.092	0.020	---	0.646	0.487	0.175	0.418	0.480
3979	8th Cell, HCl	2.765	0.028	0.102	0.018	0.005	0.011	0.002	0.384
3980	9th Cell, "	3.089	0.029	0.117	0.008	0.010	0.017	---	0.459
3981	10th Cell, "	4.350	0.022	0.167	0.011	0.014	0.018	0.001	0.546

TABLE 8.53. CONTINUED

Sample No.	Conditions, End of Run Results	Concentration in Final Composite Raffinate, gpl Fe	Cu	Zn	Cr	Ni	Al	Ca
	Seventh Day, 19 1, 6.5 hrs.							
3992	1st Stage Feed	2.299	0.013	2.084	5.510	6.520	0.013	0.008	0.510
3993	2nd Stage Feed	0.567	0.031	1.779	5.914	7.315	0.014	0.028	0.435
	Loading							
4008	1st Cell Raffinate	0.014	0.013	2.122	5.799	7.193	0.016	0.003	0.465
4009	2nd Cell Raffinate	0.014	0.041	0.455	5.799	7.298	0.008	0.003	0.417
4010	3rd Cell Raffinate	---	0.069	0.135	5.784	7.466	0.002	0.002	0.395
4011	4th Cell Raffinate	---	0.046	0.039	5.399	6.838	0.003	0.001	0.387
4022	Composite Raffinate	0.051	0.040	0.066	5.719	7.149	0.003	0.008	0.297
	Stripping							
4012	5th Cell, H_2SO_4	0.101	0.002	23.62	0.496	0.359	0.145	0.326	0.127
4013	6th Cell, "	0.088	0.016	21.51	0.472	0.345	0.139	0.316	---
1014	7th Cell, "	0.065	0.001	21.46	0.468	0.337	0.143	0.299	---
1015	8th Cell, HCl	1.705	0.012	0.049	0.008	0.020	0.010	0.010	0.127
4016	9th Cell, "	1.836	0.012	0.030	0.015	0.007	0.011	0.010	0.051
4017	10th Cell, "	2.911	0.019	0.065	0.001	0.016	0.012	0.038	0.126
	Eighth Day, 18 1, 8 hrs.							
4040	1st Stage Feed	2.040	0.019	1.987	5.338	6.030	0.017	0.019	0.530
4041	2nd Stage Feed	0.870	0.015	1.420	4.283	4.988	0.018	0.010	0.339
	Loading							
4057	1st Cell Raffinate	0.582	0.017	1.067	5.528	6.465	---	---	0.357
4058	2nd Cell Raffinate	0.133	0.019	0.231	5.300	6.313	---	---	0.307
4059	3rd Cell Raffinate	0.057	0.025	0.061	4.702	5.651	---	---	0.266

TABLE 8.53. CONTINUED

Sample No.	Conditions, End of Run Results	Concentration in Final Composite Raffinate, gpl							
		Fe	Cu	Zn	Cr	Ni	Al		Ca
4060	4th Cell Raffinate	0.039	0.022	0.023	4.969	5.798	---	---	0.251
4054	Composite Raffinate	0.028	0.015	0.043	5.478	6.707	---	---	0.463
	Stripping								
4061	5th Cell, H_2SO_4	0.136	0.020	---	0.579	0.372	---	---	0.177
4062	6th Cell, "	0.139	0.011	---	0.572	0.372	---	---	0.195
4063	7th Cell, "	0.134	0.016	---	0.544	0.366	---	---	0.153
4064	8th Cell, HCl	2.383	---	0.078	0.032	0.018	---	---	0.213
4065	9th Cell, "	2.577	0.015	0.084	0.024	0.018	---	---	0.210
4066	10th Cell, "	4.616	0.013	0.188	0.037	0.032	---	---	0.360

NOTES: 'Test conditions presented in Table 8.54.
'First day test, iron not completely oxidized; therefore, iron levels in final raffinate was high.
'Second day test, solution not doped with zinc.
'Fourth day test, iron not completely oxidized.
'Sixth day test, iron not completely oxidized.

TABLE 8.54. CONDITIONS FOR DEHPA CONTINUOUS TESTWORK TABLES

Test Series	Aqueous Volume Treated, liters		Time of Exposure, Hrs.		Initial pH	
	Day	Total	Day	Total	1st Cell	2nd Cell
First Day	19	19	14	14	1.22	1.83
Second Day	19	38	9	23	1.20	1.92 (1.48 after 1 hr.)
Third Day	19	57	6.5	29.5	1.20	1.88
Fourth Day	19	76	8	37.5	1.06	1.99
Fifth Day	20	96	7	44.5	1.10	1.86
Sixth Day	19	115	7	51.5	1.10	1.91
Seventh Day	18	133	7.5	59	1.10	1.91
Eighth Day	18	151	8	67	1.22	1.81

NOTES: ·Flow pattern presented in Figure 8.20.
·40 v/o DEHPA, 60 v/o KERMAC 510.
·O/A = 1 for both load and strip cells.
·Volume of organic in system = 7.6 Liters.
·Flow rate of organic and aqueous 40-50cc/min.
·Temperature: 20-25°C.

TABLE 8.55. CELL EFFICIENCY FOR IRON EXTRACTION BY DEHPA: LONG TERM TEST

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
	Second Day Exposure (19 1)									
3805,6	Starting solution, 2.276 gpl, Fe, 1st cell Feed, pH = 1.20; 2nd Cell Feed, pH = 1.92 initially for 1 hr. then decreased to 1.48, 1.364 gpl Fe									
3807,8,9, 10	18 Hrs.	0.400	82.4	0.088	93.5	0.055	37.5	0.055	0	96.0
3824,25, 26,27	23 Hrs.	0.515	77.4	0.234	82.8	0.146	37.5	0.109	25.3	92.0
3835	End of Run Raffinate (E.O.R.): 0.070 gpl Fe									
	Third Day Exposure (19 1)									
3846,47	Starting solution, 2.742 gpl Fe; 1st Cell Feed, pH = 1.20; 2nd Cell Feed, 1.88, 0.485 gpl									
3848,49, 50,51	26 Hrs.	1.208	55.9	0.050	89.6	0.050	0	0.050	0	89.7
3860,61, 62,63	29 Hrs.	0.854	68.9	0.055	68.9	0.018	67.3	0.027	0	94.4
3871	E.O.R. Raffinate: 0.30 gpl Fe									

TABLE 8.55. CONTINUED

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
	Fifth Day Exposure (20 l)									
3926,27	Starting Solution, 2.218 gpl Fe; 1st Cell Feed, pH = 1.10; 2nd Cell Feed, pH = 1.86, 0.509 gpl Fe									
3916,17, 18,19	41 Hrs.	1.149	48.1	0.094	81.5	0.060	36.2	0.035	41.7	93.1
3933,34, 35,36	44.5 Hrs.	1.119	49.5	0.114	77.6	0.065	43.0	0.056	13.8	89.0
3944	E.O.R. Raffinate: 0.022 gpl Fe									
	Seventh Day Exposure (18 l)									
3992,93	Starting Solution, 2.299 gpl Fe; 1st Cell Feed, pH = 1.10; 2nd Cell Feed, pH = 1.91, 0.567 gpl Fe									
4008,9, 10,11	57.0 Hrs.	0.014	99.4	0.014	0	§D.L.	100	§D.L.	100	100
4022	E.O.R. Raffinate: 0.051									
	Eighth Day Exposure (18 l)									
4040,41	Starting Solution, 2.040 gpl Fe; 1st Cell Feed, pH = 1.22; 2nd Cell Feed, pH = 1.81, 0.870 gpl Fe									

TABLE 8.55. CONTINUED

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
4042,43 44,45	62 Hrs.	----	----	0.132	84.8	0.046	65.2	0.040	13.0	95.4
4057,58 59,60	67 Hrs.	0.582	71.5	0.133	77.1	0.057	50.8	0.03	46.2	95.5
4054	E.O.R. Raffinate: 0.028 gpl Fe									

NOTES: Detailed data presented in Table 8.54.

pH of feed to cell, adjusted to 1-1.2; Raffinate fed to a separate reservor; pH of feed to Cell 2 readjusted to pH of 1.8, solution fed from reservoir to Cell 2. Usually feed for Cell 2 was raffinate from previous exposure.

Run No. 1, 4, 6 omitted because iron was not completely oxidized and DEHPA does not extract Fe^{++}.

TABLE 8.56. CELL EFFICIENCY FOR ZINC EXTRACTION BY DEHPA: LONG TERM TEST

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
	First Day Exposure (15 l)									
3745, 3789	Starting Solution, 1.828 gpl Zn 1st Cell Feed, pH = 1.22; 2nd Cell Feed, pH = 1.81, 1.070 gpl Zn									
3775,6,6,8	9 Hrs.	0.912	50.1	0.140	86.9	0.041	70.7	0.032	22.0	97.0
3795,96, 97,98	14 Hrs.	1.207	34.0	0.117	89.1	0.043	64.1	0.017	60.5	98.4
3787	End of Run (E.O.R.) Composite Raffinate: 0.080 gpl Zn									
	Third Day Exposure (19 l)									
3846,47	Starting solution, 2.207 gpl Zn 1st Cell Feed, pH = 1.20; 2nd Cell Feed, pH = 1.88, 0.299 gpl Zn									
3848,49, 50,51	26 Hrs.	1.641	25.7	0.036	88.0	0.044	----	0.059	----	80.3
3860,61, 62,63	29.5 Hrs.	0.975	55.8	0.043	85.6	0.039	9.3	0.035	10.2	88.3
3871	E.O.R. Raffinate: 0.106 gpl Zn									

TABLE 8.56. CONTINUED

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
	Fourth Day Exposure (19 1)									
3881,82	Starting solution, 2.128 gpl Zn 1st Cell Feed, pH = 1.06; 2nd Cell Feed, pH = 1.99; 1.501 gpl Zn									
3883,4,5,6	34.0 Hrs.	1.688	20.6	0.221	85.4	0.061	72.4	0.040	59.5	97.3
3895,6,7,8	37.5 Hrs.	1.427	32.9	0.270	82.0	0.082	69.3	0.038	53.7	97.5
3908	E.O.R. Raffinate: 0.046 gpl									
	Fifth Day Exposure (20 1)									
3926,27	Starting Solution, 1.999 gpl Zn 1st Cell Feed, pH = 1.10; 2nd Cell Feed, pH = 1.86; 1.636 gpl Zn									
3916,17, 18,19	41 Hrs.	1.858	14.1	0.339	79.3	0.102	69.9	0.052	49.0	96.8
3933,34, 35,36	44.5 Hrs.	1.921	3.9	0.440	73.1	0.129	70.7	0.075	41.9	95.4
3944	E.O.R. Raffinate: 0.032 gpl Zn									

TABLE 8.56. CONTINUED

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
	Sixth Day Exposure (19 1)	gpl	%	gpl	%	gpl	%	gpl	%	
3953,54	Starting solution, 2.162 gpl Zn 1st Cell Feed, pH = 1.10; 2nd Cell Feed, pH = 1.91; 1.617 gpl Zn									
3956,57, 58,59	50.5 Hrs.	1.868	13.6	0.141	91.2	0.141	0	0.054	61.7	96.7
3972,73, 74,75	51.5 Hrs.	1.527	29.4	0.383	76.3	0.108	71.8	0.046	57.4	97.2
3975	E.O.R. Raffinate: 0.050 gpl Zn									
	Seventh Day Exposure (18 1)									
3992,93	Starting Solution, 2.084 gpl Zn 1st Cell Feed, pH = 1.10; 2nd Cell Feed, pH = 1.91; 1.779 gpl Zn									
4008,9,10 11	57 Hours	2.122	0	0.455	74.4	0.135	70.3	0.039	71.1	97.8
4022	E.O.R. Raffinate: 0.066 gpl Zn									
	Eighth Day Exposure (18 1)									
4040,41	Starting solution, 1.987 gpl Zn 1st Cell Feed, pH - 1.22; 2nd Cell Feed, pH - 1.81; 1.420 gpl Zn									

TABLE 8.56. CONTINUED

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
4042,43, 44,45	62 Hrs.	----	----	0.209	85.3	0.038	81.9	0.025	34.2	98.2
4057,58 59,60	67 Hrs.	1.067	46.3	0.231	83.7	0.061	73.6	0.023	62.3	98.4
4054	E.O.R. Raffinate: 0.043 gpl Zn									

NOTES: 'Detailed data presented in Table 8.54.
'pH of feed to Cell 1 adjusted to 1-1.2; raffinate fed to a separate reservoir; pH of feed to Cell 2 readjusted to 1.8.
'Run No. 2 omitted because zinc content very low.

TABLE 8.57 CELL EFFICIENCY FOR IRON AND ZINC EXTRACTION BY DEHPA: LONG TERM TEST

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
	(See Tables 8.55, 8.56)									
	Third Day Exposure									
3848,49 50,51	26 Hrs.	2.849	42.4	0.086	89.0	0.090	----	0.109	----	86.1
3860,61 62,63	29.5 Hrs.	1.829	63.0	0.098	87.5	0.057	41.8	0.062	----	92.1
3871	End of Run (E.O.R.) Raffinate: 0.137 gpl Fe + Zn									
	Fifth Day Exposure									
3916,17, 18,19	41 Hrs.	2.197	47.9	0.433	79.8	0.162	62.6	0.087	46.3	95.9
3933,34 35,36	44.5 Hrs.	3.040	27.9	0.554	74.2	0.194	35.0	0.131	32.5	93.9
3944	E.O.R. Raffinate: 0.053 gpl Fe + Zn									
	Seventh Day Exposure									
4008,9, 10,11	57 Hrs.	2.136	51.3	0.469	80.0	0.135	71.2	0.039	71.1	98.3
4022	E.O.R. Raffinate: 0.117 gpl Fe + Zn									

TABLE 8.57. CONTINUED

Sample No.	Conditions	Cell Efficiency, gpl in Raffinate, % Extracted								Total Efficiency
		Cell 1		Cell 2		Cell 3		Cell 4		
		gpl	%	gpl	%	gpl	%	gpl	%	
	Eighth Day Exposure									
4042,43 44,45	62 Hrs.	----	----	0.341	85.1	0.084	75.4	0.065	22.6	97.2
4057,58 59,60	67 Hrs.	1.649	59.1	0.341	85.1	0.084	75.4	0.065	22.6	97.2
4054	E.O.R. Raffinate: 0.071 gpl Fe + Zn									

NOTES: *See Tables 8.54, 8.55, and 8.56.

carried over to the other extraction cells and into the strip cells thereby contaminating the strip solution; and excessive loss of organic occurred.

An analyses of the crud material showed high iron and phosphorus contents. Therefore, a series of tests were conducted to investigate the role of iron content in the aqueous phase. The experimental approach consisted of:

- cleaning out the Reister SX testrack; refilling with new 40 v/o D_2EHPA, 60 v/o KERMAC 470B, 200 gpl H_2SO_4 strip acid (3 cells) and 4 N HCl strip acid (1 cell).

- exposing the new organic and strip solutions to first pure zinc sulfate solutions; then to a low iron bearing feed; then to a mixed metal feed. An organic/aqueous ratio of one was maintained in all extraction and strip cells. (The flow pattern is presented in Figure 8.15.)

ZINC SULFATE TEST RESULTS

Conditions: 75 liters feed solution, 2.46 gpl Zn.

Unused 40 v/o D_2EHPA, 60 v/o KERMAC 470B; volume = 32.8 liters.

Unused 200 g/l H_2SO_4 acid doped with $ZnSO_4$ to Zn concentration = 30.4 g/l, volume = 12.0 liters.

Unused 4 N HCl in rack, volume = 4.1 liters.

Cells 1, 2, 3, 4 feed rate maintained @ 0.25 l/min.

Cell 1 feed @ pH = 2.0

Cell 3 feed @ pH = 2.0, adjusted with 500 g/l KOH.

Strip acid was replaced hourly to maintain acid concentration at 200 gpl.

Method: Evaluation of crud formation was strictly by observation with most attention given to cell #1 settler. Crud formation was judged critical when:

1. interface level in cell #1 became uncontrollable, caused by crud clogging aqueous jack-leg line.
2. crud overflowed organic weir for transport to strip section with subsequent contamination of strip acid.

Results: Chemical results for the test series are presented in Table 8.58.

TABLE 8.58. ZINC SULFATE SOLUTION CRUD FORMATION TEST: Zn RECOVERY

Condition	Zinc Concentration in Aqueous Phase (gpl)	
	Cell 2	Cell 4
Starting Solution, 75 liters 2.46 gpl Zn, pH = 1.96.		
Raffinate		
45 min.	0.56 (pH = 1.36)	
2 Hrs	0.52	
3 Hrs	0.41 (pH = 1.37)	0.02
4 Hrs	0.22 (pH = 1.35)	0.01

Notes:
- Test conducted in large scale Reister SX testrack.
- See text for test conditions.

Comments: First stage extraction cell #1 showed considerable crud formation approximately half-way through the run; temperature of feed solution was at 22.0 C. Feed solution was heated to approximately 40°C, and although crud did not dissipate, it did stop increasing in amount.

Strip acid replacement was performed entirely in strip cell #3 settler. Evaluation of Zn concentration in each strip cell at end of run showed significant differences in Zn concentration between cells, which was assumed to correspond inversely to H_2SO_4 concentrations. Strip acid flow rates between cells were approximately 0.2 liters/min. allowing for approximately two cell volumes of aqueous per hour through each cell. Obviously this was insufficient volume change to distribute new acid throughout the strip system each hour. Based on this observation, acid replacements in all subsequent experiments was performed by equal volume replacement in each strip cell settler. Strip acid replacement calculation was based on 3.0 g/l Zn in feed solution when actual Zn concentration in feed was 2.46 g/l. this resulted in over-dilution of Zn concentration in strip acid through course of this experiment. End of run data indicated Zn average concentration to be 24.7 g/l instead of projected 30.4 g/l.

MIXED METAL FEED SOLUTION TEST RESULTS

Purpose of Experiment:

Provide mixed metal feed solution to ZnSX system and monitor crud formation. Evaluate effectiveness of equal volume strip acid replacement in each strip cell settler.

Conditions: 75 liters mixed metal leach solution produced from Norris Industries sludge; i.e., 4470 g sludge, 740 ml H_2SO_4, diluted to 75 liters with DI water.

D_2EHPA from previous test.

H_2SO_4 strip solution left from previous test; 24.75 gpl Zn; volume = 12.0 liters, three H_2SO_4 strip cells.

HCl volume increased for this run by placement of an external reservoir of 4N HCl, total volume HCl = 19.1 liters, one HCl strip cell.

Cells 1, 2 ,3, 4 feed rate @ 0.25 liters/min.

Cells 1 and 2 feed pH = 2.0.

Cells 3 and 4 feed pH = 2.0, adjusted with 500 g/l KOH.

Method: Evaluation of crud formation same as for zinc sulfate solution test.

Results: Chemical results for the test series are presented in Table 8.59.

Comments: Crud formation with this feed was more severe than that encountered with the previous run. Crud in cell #1 settler was removed after 4 1/2 hours of system operation (i.e., 90% of feed volume through cell #1) because crud began overflowing organic weir.

Evaluation of strip section, cell-by-cell Zn concentrations showed equal volume acid replacements in each settler to be effective in reducing differences in Zn concentrations between cells.

Assay of HCl strip showed practically no Fe content at end of experiment; also HCl strip showed no yellow color characteristic of even low concentration of $FeCl_3$. Conclusion drawn was that HCl used to mix strip had previously been diluted, resulting in a strip solution far below 4 N in HCl concentration.

MIXED METAL FEED SOLUTION TEST RESULTS, HIGH IRON

Purpose of Experiment:

Test crud formation in ZnSX system with a high iron bearing, mixed-metal feed solution.

Conditions: 75 liters mixed-metal leach solution produced from Norris Industries sludge; i.e., 4470 g sludge, 740 ml H_2SO_4, diluted to 75 liters with DI water. Ferrous sulfate added to bring Fe content of feed up to 3.0 g/l. H_2O_2 added to oxidize Fe^{+2} to Fe^{+3}.

D_2EHPA from previous test.

H_2SO_4 strip replacement scheme as before, volume of strip = 12.0 liters.

HCl from previous test replaced with 4 N HCl solution made from reagent grade HCl, 18.0 liters in system, one HCl strip cell with external reservoir.

Cells 1, 2, 3, 4 feed rate @ 0.25 liters/min.

Cells 1 and 2 feed @ pH = 2.0.

Cells 3 and 4 feed @ pH = 2.0, adjusted with 500 g/l KOH.

Method: Evaluation of crud formation same as for previous test.

Results: Chemical results for the test series are presented in Table 6.60.

Comments: Crud formation for this run was extreme. Cell #1 of first extraction stage became uncontrollable after 35 liters of feed

TABLE 8.59. MIXED METAL SOLUTION CRUD FORMATION TEST: IRON AND ZINC RECOVERY

Conditions	Metal Concentration in Aqueous Phase (gpl)			
	Cell 2		Cell 4	
Starting Solution, 75 liters 0.33 gpl Fe, 2.74 gpl Zn, 1.80 gpl Cr, pH = 1.95.				
Raffinate	Fe	Zn	Fe	Zn
1.5 Hrs	< D.L.	0.16	-	-
2.5	< D.L.	0.13	<D.L.	0.01
4.0	< D.L.	0.11	<D.L.	0.01
5.0	< D.L.	<D.L. (pH:1.34)	<D.L.	< D.L. (pH:1.63)

Notes: . See text page 283 for conditions.
. Test conducted in large scale Reister SX testrack.

TABLE 8.60. HIGH IRON MIXED METAL SOLUTION CRUD FORMATION TEST: IRON AND ZINC RECOVERY

Conditions	Metal Concentration in Aqueous Phase (gpl)					
	Cell 2			Cell 4		
Starting Solution, 75 liters 2.71 gpl Fe, 2.68 gpl Zn, 1.63 gpl Cr, pH = 2.03						
Raffinate	Fe	Zn	Cr	Fe	Zn	Cr
1.5 Hrs	0.01	0.33	1.78	< D.L.	0.01	1.66
	(pH = 1.63)					
3.0	< D.L.	0.91	-	< D.L.	0.01	-
	(pH = 1.24)			(pH = 1.59)		

Notes:
- See text page 283 for conditions.
- Test conducted in large scale Reister SX testrack.

because jack-leg plugged with crud. Experiment was halted, cell #1 settler cleaned of crud, and temperature of the feed increased from 20°C to 45°C. Operation continued with only a slight decrease in crud formation rate.

Cell #1 of the first stage extraction appeared to be removing a good portion of the Fe present in the feed solution. Color change between cell #1 feed and cell #1 raffinate led to this suspicion. The feed stream was dark green in color; characteristic of a high Fe bearing solution, and the raffinate stream from cell #1 was light blue in color: characteristic of the Norris sludge leach solution before Fe addition.

8.4.3.2. Crud Problem Solution

The crud formation problem was overcome by switching the kerosene diluent. KERMAC 510 was substituted for the previously used KERMAC 470B. A comparative analysis between the two kerosenes is presented in Table 8.61. The major difference is the aromatic content, i.e., 470B has a nominal 11.7% aromatic content, 510 has a nominal 2.5% aromatic content.

All subsequent testwork was performed using 510 as the diluent. The long-term continuous testwork was initiated using 470B. Crud formation was initially a problem in that test set-up (Bell Engineering Testrack) but the problem disappeared when the diluent was switched from 470B to 510. Phase separation, metal value selectivity, metal value recovery (Zn plus Fe), and interface control were excellent throughout the test series.

8.5. SOLID-LIQUID SEPARATION

An Ingersol-Rand 360 IX LASTA pilot scale filter press (shown pictorally in section 8.14) was purchased for the project. The particular press system was chosen so that a number of experimental variables could be investigated, e.g., cake compression, wash options, flow rates, back pressures, temperature, filter cloth porosity, air drying. Extensive investigation to establish optimum filtering conditions has not been performed. Filter press features are presented in Table 8.62.

The filter press has been used on large scale tests to separate the jarosite-leach residue solid mixture from the solution. Tests have been performed on filterability of leach residue and on mixtures of jarosite-leach residues. Typical results are summarized in Table 8.63.

TABLE 8.61. COMPOSITION OF DILUENT USED FOR DISSOLUTION OF DEHPA

Diluent	Composition, %		
	Paraffins	Naphthalenes	Aromatics
KERMAC 470B	48.6	39.7	11.7
KERMAC 510	----	----	2.5

NOTES: *Composition was not determined during this study. Values reported are from literature sources (Ref. 28).

TABLE 8.62. PILOT SCALE IR LASTA FILTER PRESS

Material of Construction:	All wetted parts 316SS except diaphrams are natural rubber
Filtering Area:	0.104 M^2 (2.2 $ft.^2$)
Chamber Volume:	1.2 liters (0.3 gal.)
Pressure:	
Feed Solution	7 kg/cm^2 (99.5 psi)
Compression water for diaphragm testing	15 kg/cm^2 (213 psi) to 20 kg/cm^2 (284 psi)

The filtering rate for a jarosite solid is much greater than the filtering rate of the leach residue. This is, in fact, one of the main reasons for removing iron as a jarosite, i.e., the ease in solid/liquid separation.

The jarosite filtering rates achieved in this study are compared to commercial filtration data supplied by Ingersol-Rand, Table 8.64.

TABLE 8.63. FILTERABILITY TESTWORK

Leach Residue: Test 29-2

Operating Sequence	Time (min.)	Volume Liquid Recovered (liters)	Suspended Solid (mg/l)
Feed	7	3.2	75
Core Blow	0.3	---	
Top Wash	3	1.7	)
Precompression	1	0.9	) Composite 140
Backwash	3	1.1	)
Compression	5	0.5	)

Resulting cake moisture (average of three separate press tests): 46.4% solids.
Solid loading rate (average of three separate press tests): 4.5 kg/m^2/hr.

Jarosite-Leach Residue Mixture

Feed Test No.	Time (min.)	Volume Liquid Recovered (liters)	Suspended Solid (mg/l)
5-1	6	20.1	---
5-2	8	39.1	---
5-3	13	20.6	---
5-4	11	15.9	---
5-5	9	13.9	---
Top Wash Test			
5-1	4	18.3	---
5-2	4	3.9	---
5-3	---	3.0	---
5-4	4	2.3	---
5-5	4	2.4	---

Resulting Cake Moisture and Loading Rate

Test No.	% Solids	Loading Rate kg/m^2/hr.
5-1	67.9	54.0
5-2	68.6	41.0
5-3	71.2	26.3
5-4	66.9	29.1
5-5	66.2	35.1

TABLE 8.64. JAROSITE FILTRATION RATES

	Present Study	Japan*	Canada*
Feed Solids	40-50	50-55	20-30
Solids Loading Rate (kg/m^2/hr.)	25-55	80-100	40-50
Cake Solids (%)	66-71	78-80	75-78

*data supplied by Ingersoll-Rand(46)

Settling rates are exceptionally rapid for jarosite solids. The experimental solid/liquid separation in the large scale testwork was, in fact, accomplished by allowing the solids to settle; pumping a major portion of the liquid out of the leach vessel; then filter pressing the remaining slurry. These tests were performed in a 270 liter vessel containing about 200 liters of solution plus solids. The jarosite settling was essentially complete in less than 30 minutes.

8.6. COPPER SOLVENT EXTRACTION TESTWORK

8.6.1. Small Scale Preliminary Testwork

A large number of preliminary small scale shake tests were performed to characterize several commercially used copper extractant reagents, LIX-64N, LIX-622.

8.6.1.1. LIX 64N

Preliminary shake tests were conducted to establish potentially important variables and experimental procedure. The design matrix that was developed from preliminary tests is presented in Table 8.65. The results show that copper extraction is primarily a function of LIX-64N content, and leach solution pH and that the presence of deconol decreases copper extraction. The other variables have minimal influence on copper extraction. The effects portion of the table indicates that none of the six variables studied greatly influence the extraction of other elements. Conditions can be chosen from the design table matrix to achieve effective and selective copper extraction.

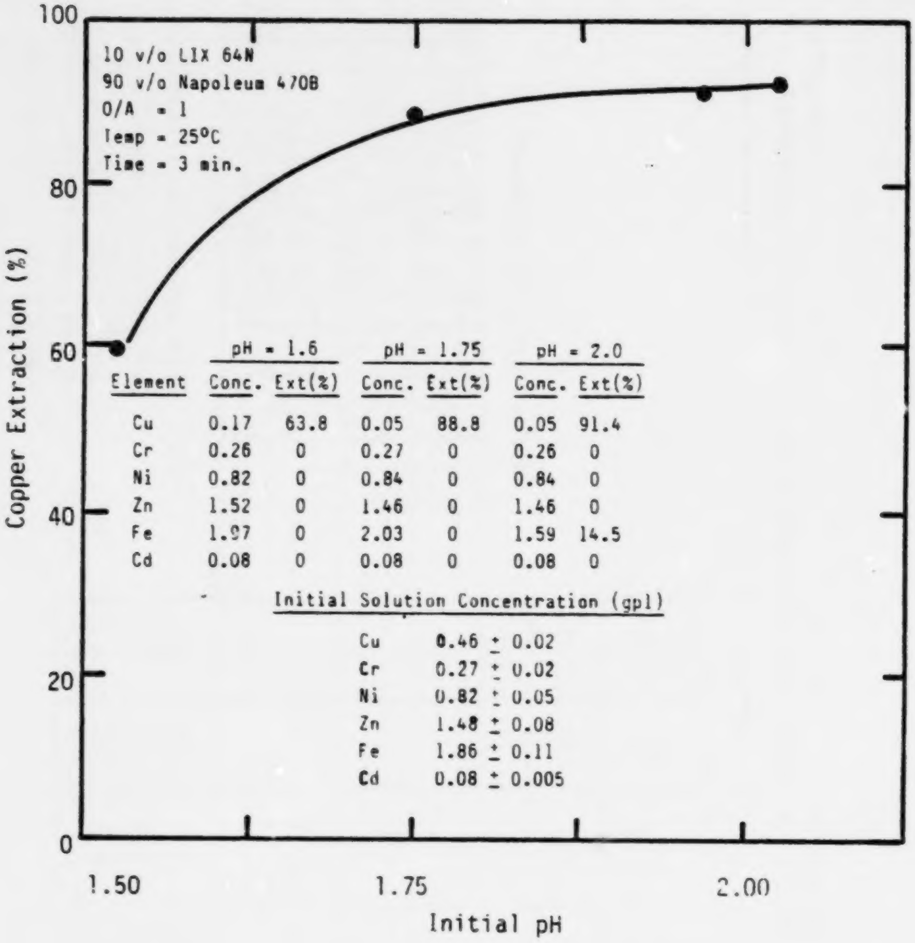
A number of other tests were conducted using the LIX-64 reagent. The influence of pH on copper extraction (other metal extractions are shown in a data table on the same figure) is presented in Figure 8.16. Copper is preferentially extracted from the leach solution at pH values up to 1.75, i.e., Cr, Ni, Zn, Fe, and Cd are not extracted. Some iron was extracted at a pH of 2 and above. Note, however, that in these tests there was a large excess of LIX-64 reagent above what is required to remove the low copper content, i.e., further experimental work showed that approximately 0.1 gpl Cu is removed from

TABLE 8.65. DESIGN MATRIX FOR LIX 64N EXTRACTION OF COPPER FORM SLUDGE LEACH SOLUTION (1/8 REPLICA)

Results - Extraction by Organic (%)

Sample		LIX 64N (%)	Type Kerosene	Deconol (%)	Time (min.)	Temp. (°C)	Leach Solution pH							
	Base	15	470B	10	3	40	1.75							
	Unit	5	--	10	2	15	0.25							
	High (+)	20	470B	20	5	55	2.0							
	Low (-)	10	450	0	1	25	1.5							
	Test #								Cu	Fe	Cr	Ni	Zn	Cd
279	1	-	-	-	-	-	-		31.6	10.5	3.3	9.6	42.8	8.6
280	2	+	-	-	+	-	+		98.2	17.5	4.6	13.0	10.0	7.4
281	3	-	+	-	+	+	-		51.8	2.5	0	2.8	1.4	1.2
282	4	+	+	-	-	+	+		95.1	19.0	5.8	8.5	8.6	9.8
283-7	5	-	-	+	+	+	+		4.1(8.6	29.6 (27.7)	14.0(14.0	5.8(1.1)	2.1(4.3)	8.6(8.6)
284	6	+	-	+	-	+	-		4.2	0	0	1.7	12.1	0
285	7	-	+	+	-	-	+		14.7	15.5	5.0	8.5	2.1	8.6
286	8	+	+	+	+	-	-		13.3	12.0	2.5	9.6	3.6	8.6
288-90	Baseline								49.3±9.1	6.5 ± 1.0	5.7±1.7	8.5±2.3	8.6±0.8	9.8±2.5
								Max. Exp. Variation	±9.1	±2.6	±3.2	±4.7	±2.6	±5.6
	Effects													
	Cu	10.4	1.4	-26.9	5.9	2.9	17.1							
	Fe	0.8	0.9	- 1.0	0.1	-2.5	5.1							
	Cr	0.6	0.7	- 0.8	-0.9	-1.2	1.2							
	Ni	0.4	-0.4	- 0.7	0.7	-2.4	1.8							
	Zn	- 2.8	-7.4	-4.4	-5.1	-3.3	- 3.6							
	Cd	- 0.2	0.5	-0.2	-0.2	-1.7	+ 2.0							

NOTE:
- ·Leach Solution from Sludgebarrel 1
- ·Initial Solution Composition (gpl)
  Cu 0.45 ± 0.01, Cr 0.24 ± 0.02,
  Zn 1.40 ± 0.03, Fe 2.00 ± 0.04,
  Ni 0.86 ± 0.03, Cd 0.081± 0.002
- ·Organic/Aqueous = 1: 50cc each
- ·Test 5 Duplicated
- ·Baseline Run Three Times



	pH = 1.6		pH = 1.75		pH = 2.0	
Element	Conc.	Ext(%)	Conc.	Ext(%)	Conc.	Ext(%)
Cu	0.17	63.8	0.05	88.8	0.05	91.4
Cr	0.26	0	0.27	0	0.26	0
Ni	0.82	0	0.84	0	0.84	0
Zn	1.52	0	1.46	0	1.46	0
Fe	1.97	0	2.03	0	1.59	14.5
Cd	0.08	0	0.08	0	0.08	0

Initial Solution Concentration (gpl)

Cu	0.46 ± 0.02
Cr	0.27 ± 0.02
Ni	0.82 ± 0.05
Zn	1.48 ± 0.08
Fe	1.86 ± 0.11
Cd	0.08 ± 0.005

Figure 8.16. Influence of pH on LIX 64N extraction

a leach solution by each volume percent (v/o) of LIX-64 reagent; Table 8.66. This means then, that an excess amount of LIX-64N was present in the isotherm tests and that other cations may be picked up (at the higher pH levels) once the copper is removed from the solution. A better designed experiment would have been to expose the solution to an organic phase of about five v/o LIX-64N.

The influence of LIX-64 concentration on metal extraction at a fixed pH is presented in Figure 8.17. McCabe-Thiele equilibrium extraction isotherms, pH 1.98 and pH 2.20, are presented in Figures 8.18 and 8.19. The experimental data developed for the McCabe-thiele diagrams are presented in Tables 8.67, and 8.68. The reader should note that the data reinforces the previous conclusion that LIX-64 reagent is, indeed, very selective toward copper.

The above described tests were conducted on low copper containing solutions. Shake tests were also performed on high copper (4.86 gpl) solutions at various O/A ratios and pH levels. The results are presented in Table 8.69. The copper content is not extracted from the aqueous phase to low levels because the LIX-64N content (40 v/o) will only extract 0.06-0.1 gpl Cu per v/o reagent, i.e.,∿ 4 gpl. (The copper loading into the organic achieved in the present study was only about one-half the loading quoted by Henkel Corporation in their literature, i.e., 0.25 gpl Cu / v/o LIX-64N. The reason for this difference is presently unexplained.)

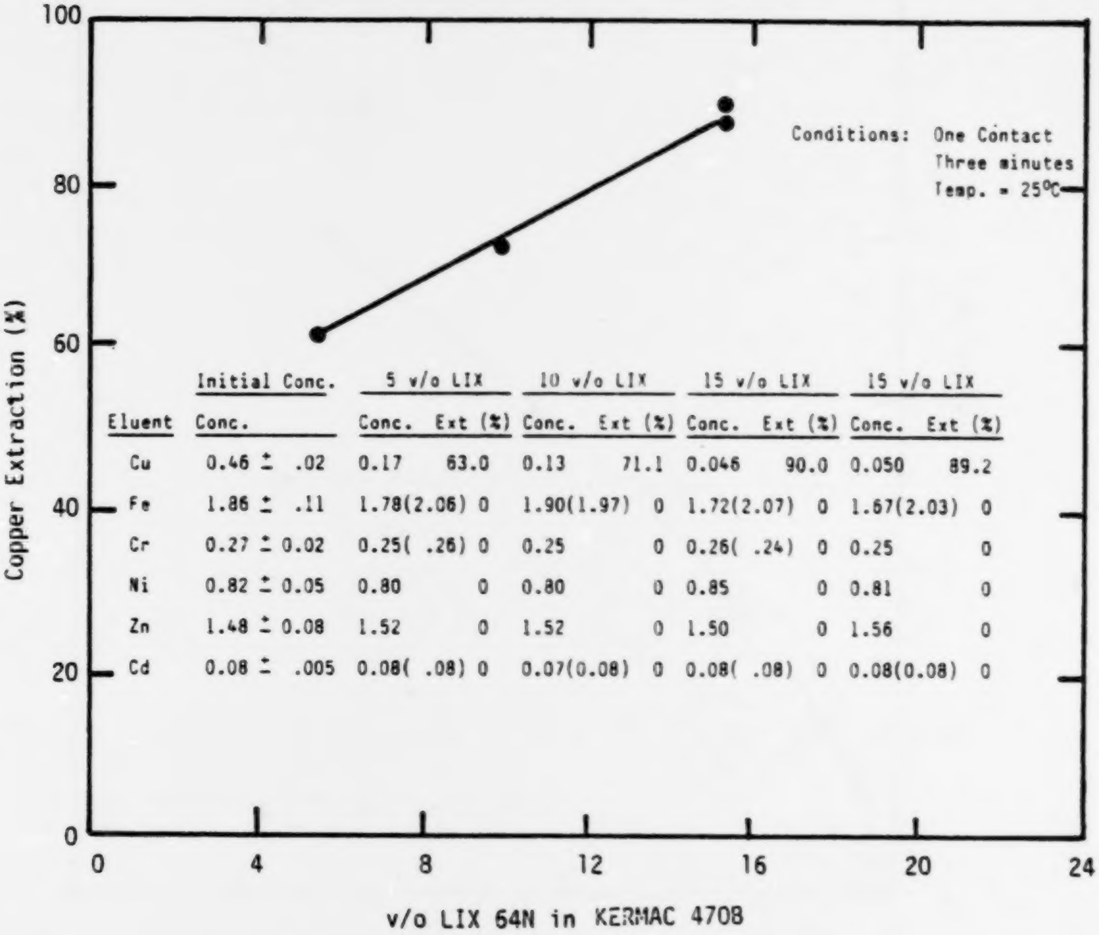
The successful extraction of copper by LIX-64N was further demonstrated in a larger scale test, i.e., ten liters of leach solution was treated in a three-stage continuous (600cc mixer, 100cc/minute flow rate) system (Bell Engineering unit). Three stages of organic loading was followed by two stages of organic stripping. The test conditions and results are presented in Table 8.70.

Copper extraction using LIX-64N is commercially only practiced for low concentration solutions, i.e.,∿ 2 gpl Cu, and LIX-64N contents seldom exceed 10-12 v/o. The present study deals with copper contents usually greater than 2 gpl Cu. Therefore, one should consider the reagents that are designed for higher copper loading, such as, ACORGA 5100 or LIX-622 reagents. Experiments were conducted with both ACORGA 5100 and LIX-622. LIX-622 was chosen for large scale Cu SX test work but ACORGA 5100 would also be appropriate. The procedure

TABLE 8.66. SUMMARY OF COPPER LOADING IN LIX 64 N (40v/o)-KERMAC 470B

	gpl Cu / v/o LIX 64N					
	O/A					
Initial pH	10	5	2	1	0.5	0.2
pH = 1.50	0.09	---	---	0.06	---	0.02
pH = 1.75	0.09	0.10	0.10 (0.10)	0.08	0.06 (0.06)	0.03
pH = 2.00	0.11	---	---	0.10	---	0.04

NOTE: . Maximum copper loading 6.6 gpl.



	Initial Conc.	5 v/o LIX		10 v/o LIX		15 v/o LIX		15 v/o LIX	
Eluent	Conc.	Conc.	Ext (%)	Conc.	Ext (%)	Conc.	Ext (%)	Conc.	Ext (%)
Cu	0.46 ± .02	0.17	63.0	0.13	71.1	0.046	90.0	0.050	89.2
Fe	1.86 ± .11	1.78(2.06)	0	1.90(1.97)	0	1.72(2.07)	0	1.67(2.03)	0
Cr	0.27 ± 0.02	0.25(.26)	0	0.25	0	0.26(.24)	0	0.25	0
Ni	0.82 ± 0.05	0.80	0	0.80	0	0.85	0	0.81	0
Zn	1.48 ± 0.08	1.52	0	1.52	0	1.50	0	1.56	0
Cd	0.08 ± .005	0.08(.08)	0	0.07(0.08)	0	0.08(.08)	0	0.08(0.08)	0

Figure 8.17. Influence of LIX 64N concentration at pH = 1.76.

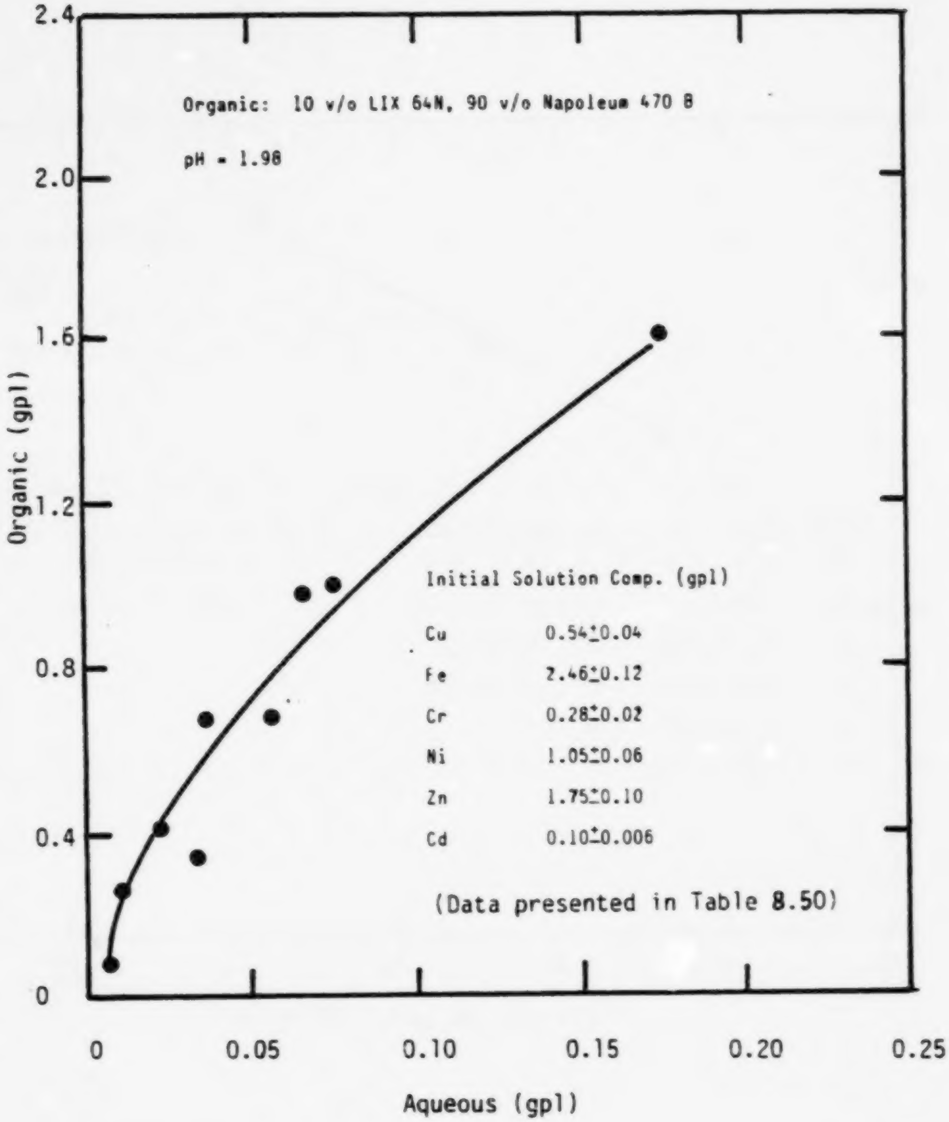


Figure 8.18. McCabe-Thiele equilibrium extraction isotherm: LIX 64N, pH = 1.98.

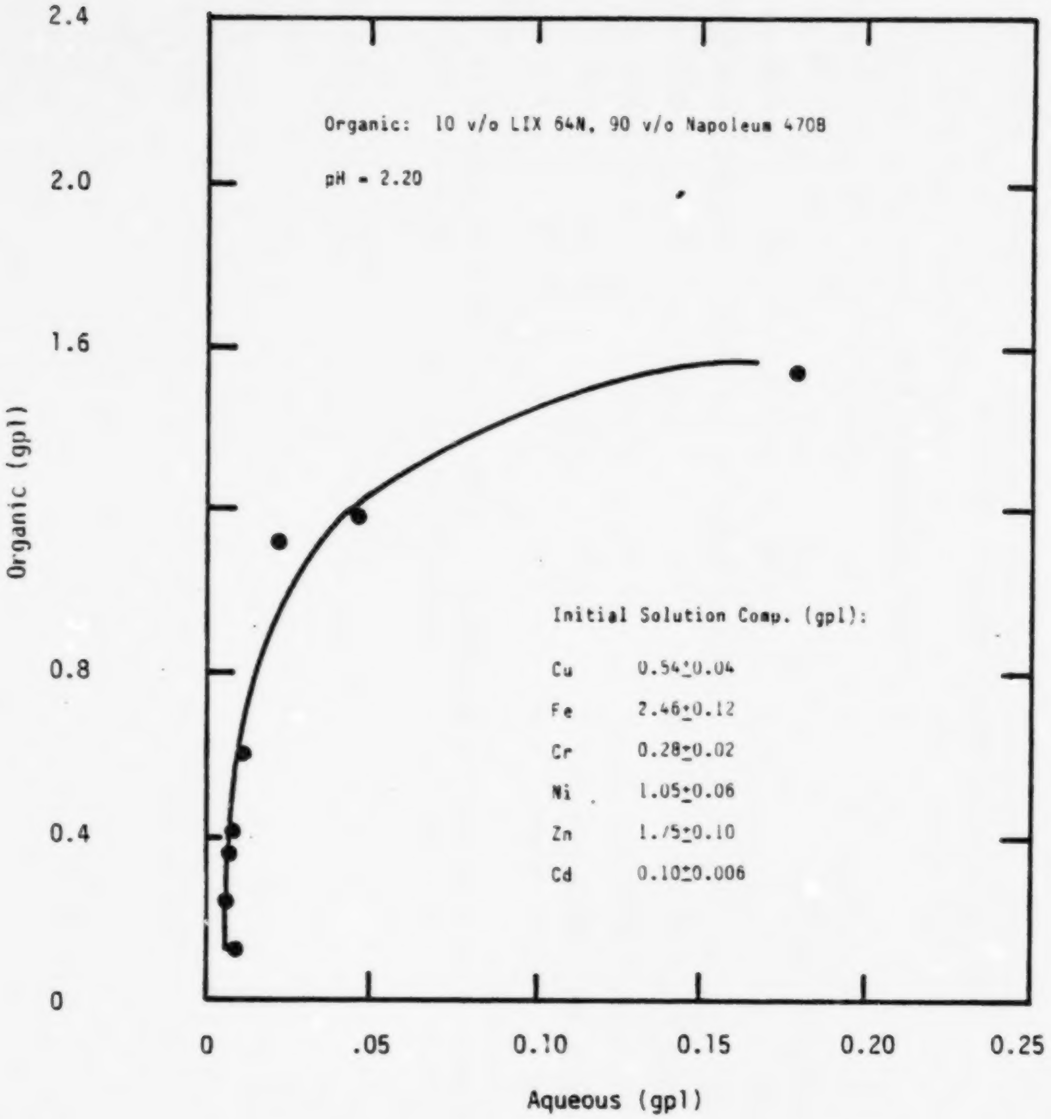


Figure 8.19. McCabe-Thiele equilibrium extraction isotherm: LIX 64N, pH = 2.2.

TABLE 8.67. McCABE-THIELE DIAGRAM DATA: pH = 1.98

O/A Ratio	Element Concentration (gpl)						
	Cu		Aqueous				
	Organic	Aqueous	Fe	Cr	Ni	Zn	Cd
10	0.060	---	2.26	0.26	0.94	1.66	0.09
5	0.256	0.011 (0.018)	--- (2.16)	0.24 (0.25)	0.87 (0.95)	1.46 (1.60)	0.09 (0.09)
2	0.376 (0.402)	0.035 (0.031)	2.26	0.26	0.95	1.64	0.09
1	0.670 (0.670)	0.058 (0.032)	2.19	0.25	0.96	1.60	0.09
0.5	1.004 (0.996)	0.065 (0.074)	2.29	0.26	0.94	1.66	0.09
0.2	1.600	0.175 (0.196)	2.35	0.26	0.97	1.70	0.09

Starting solution (gpl): 0.54±0.04 Cu, 2.46±0.12 Fe, 0.28±0.02 Cr, 1.05±0.06 Ni, 1.75±0.10 Zn, 0.10±.006 Cd.

TABLE 8.68. McCABE-THIELE DIAGRAM DATA: pH = 2.20

O/A Ratio	Element Concentration (gpl)						
	Cu		Aqueous				
	Organic	Aqueous	Fe	Cr	Ni	Zn	Cd
10	0.143	0.009	2.18	0.25	0.95	1.62	0.09
5	0.234	0.005 (0.008)	2.13	0.24 (.25)	0.86 (0.92)	1.60 (1.58)	0.08 (.08)
2	0.400 (0.378)	0.007 (0.007)	2.10 (2.17)	0.24 (.25)	0.90 (0.94)	1.55 (1.60)	0.08 (0.09)
1	0.596	0.011	2.23	0.25	0.96	1.65	0.08
0.5	1.166 (1.111)	0.049 (0.022)	2.16 (2.19)	0.25 (.25)	0.91 (0.94)	1.58 (1.60)	0.08 (0.09)
0.2	1.540	0.179 (0.176)	2.21	0.25	0.94	1.62	0.09

Starting solution (gpl): 0.54±0.04 Cu, 2.46±0.12 Fe, 0.28±0.02 Cr, 1.05±0.06 Ni, 1.75±0.10 Zn, 0.10±0.006 Cd.

TABLE 8.69. LIX 64N ISOTHERM DATA: 40 v/o LIX 64N APPLIED TO LEACH SOLUTION

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Ni	Cr	Cd	Al
1061	Starting Solution	4.86	15.16	10.34	4.12	1.04	0.58	4.71
	pH = 1.75							
1064	0/A = 5	0.82	14.68	10.02	4.04	1.02	0.57	4.58
1065	0/A = 2	0.90	14.32	9.76	3.97	1.00	0.56	4.46
1069	0/A = 2 (repeat)	0.87	14.59	9.87	4.06	1.02	0.57	4.53
1066	0/A = 1	1.52	14.58	9.88	4.06	1.01	0.57	4.50
1067	0/A = 0.5	2.34	14.97	10.16	4.18	1.04	0.59	4.67
1070	0/A = 0.5 (repeat)	2.37	15.22	10.31	4.24	1.06	0.60	4.72
1068	0/A = 0.2	3.54	15.23	10.32	4.26	1.06	0.60	4.73
	pH = 1.5							
1071	0/A = 10	1.22	14.64	9.92	4.04	1.02	0.57	4.53
1072	0/A = 1	2.28	15.20	10.27	4.23	1.05	0.60	4.66
1073	0/A = 0.2	3.97	15.06	10.15	4.17	1.04	0.59	4.62

TABLE 8.69. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Ni	Cr	Cd	Al
	PH = 2.0							
1074	O/A = 10	0.34	15.38	10.44	4.26	1.07	0.61	4.80
1075	O/A = 1	0.94	15.40	10.45	4.38	1.08	0.62	4.72
1076	O/A = 0.2	3.36	16.07	10.81	4.49	1.11	0.64	4.93

NOTE: ·Organic phase: 40 v/o LIX 64N, 60 v/o 470B contacted with leach solution (892) to pre-condition; then stripped with synthetic electrolyte solution (30 gpl Cu, 180 gpl H_2SO_4).

·All contacts performed for 3 minutes at 20°C.

TABLE 8.70. CONTINUOUS COPPER EXTRACTION FROM MIXED METAL LEACH SOLUTION BY LIX 64N

Organic Phase: 10 v/o LIX-64N; 90 V/O KERMAC 470-B

Aqueous Phase Composition (gpl):	Cu	Fe	Cr	Ni	Zn	pH
	2.80	7.03	0.64	6.86	8.13	Adjusted to 2

Loading Contacts	3, 0/A = 1
Stripping	2, 0/A = 10
Flow Rate	100 cc/min.
Volume Treated	10 liters
Copper Content of the Raffinate	11 ppm
Copper Content of the Strip Solution	4.96 gpl
Acid in Strip	20 v/o H_2SO_4

used to develop the isotherm data followed that prescribed by Henkel Corporation (30): The organic solution is loaded with a little copper by contacting it with feed in a separatory funnel. Next, the organic is shaken with a typical tankhouse electrolyte (30 g/l Cu, 150 g/l H_2SO_4) at an O/A = 1. This pre-prepared organic is then contacted with aqueous leach solution at various O/A ratios. The two phases are recovered and analyzed.

8.6.1.2. LIX-622

LIX-622 is a reagent developed by Henkle Corporation for copper extraction applications under acid conditions where the pH <1.5 and where the copper content is rather high, i.e., and >2 gpl. The design matrix results (Table 8.71. and 8.72.) verify that effective copper extraction occurs within the pH range 1.0-1.5. The effect of pH (in the range 1-1.5) is not very important with respect to copper extraction, but it is important to keep the pH low in order to minimize the extraction of other elements (which does occur to a greater extent as pH is raised). From the effects portion of the design matrix table it appears that pH is the only important variable influencing extraction of elements other than copper.

TABLE 8.71. DESIGN MATRIX FOR LIX-622 EXTRACTION OF COPPER FROM SLUDGE LEACH SOLUTION (1/2 REPLICA)

Sample		LIX 622 (%)	Type Kerosene	Deconol (%)	Mix Time (min.)	Mix Temp. (°C)	Leach Solution pH
	Base	15	470-B	10	3	40	1.25
	Unit	5	---	10	2	15	0.25
	High (+)	20	470-B	20	5	55	1.5
	Low (-)	10	450	0	1	25	1.0
	Test No.						
344	1	-	-	-	-	-	-
345	2	+	-	-	+	-	+
346	3	-	+	-	+	+	-
347	4	+	+	-	-	+	+
348	5	-	-	+	+	+	+
349 &	52 6	+	-	+	-	+	-
350	7	-	+	+	-	-	+
351	8	+	+	+	+	-	-
353-5	Base						
	Effects						
	Cu	0.2	-4.5	-14.0	4.8	-0.2	0.5
	Fe	-0.1	-1.1	0.9	-0.4	-1.8	9.6
	Cr	-0.4	-1.1	- 1.1	-0.4	-2.4	9.4
	Ni	-0.1	-0.9	- 1.1	-0.4	-2.1	9.6
	Zn	-0.2	-1.0	- 0.8	-0.5	-1.8	9.5
	Cd	-1.0	-1.0	- 1.0	-1.0	-3.0	9.5

Results: Extraction from Solution (%)

	Cu	Fe	Cr	Ni	Zn	Cd
	88.0	15.0	14.0	11.0	15.0	8.0
	97.0	33.0	31.0	29.0	32.0	25.0
	86.0	8.0	6.0	4.0	8.0	0.0
	80.0	28.0	25.0	24.0	28.0	0.0
	70.0	28.0	25.0	23.0	28.0	17.0
	58.0	9.0(10.0)	6.0(6.0)	4.0(4.0)	9.0(9.0)	0.0(0.0)
	50.0	30.0	28.0	26.0	30.0	25.0
	61.0	10.0	8.0	6.0	10.0	0.0
	87.0±4.0	12.0±1.0	10.0±2.0	7.0±1.0	12.0±2.0	0.0±0.0
Max. Exp. Variation	± 4.6	± 8.3	± 6.5	±1.0	± 6.0	± 6.5

NOTE:
- Sludge Type 2
- Initial Solution Composition (gpl): 0.66 Cu, 3.18 Fe, 0.36 Cr, 1.37 Ni, 2.29 Zn, 0.12 Cd
- Organic/Aqueous = 1; 50cc each
- Test 6 duplicated
- Baseline run three times

TABLE 8.72. OBSERVATIONS ON PHASE SEPARATION: DESIGN MATRIX TESTS (TABLE 8.54) FOR COPPER REMOVAL USING LIX 622

Test #	Observations
1	Good Separation
2	Fair Separation, Mucky*
3	Good Separation
4	" "
5	" "
6	" "
6b	" "
7	" "
8	" " , Little Muck
Baseline A	" " , But Some Muck
Baseline B	" " " " "
Baseline C	" " " " "

*Muck: A layer of organic-aqueous that disappears slowly.

The design matrix study approach should only be considered a qualitative evaluation of system experimental variables. The interpretation should be limited to pointing out parameters that have a large effect on element recovery. The design matrix results show reasonably high metal value extraction of associated elements. This result, however, is due to the fact that the tests were conducted prior to establishing the extraction ability of the LIX-622 reagent, i.e., the extraction ability of LIX-622 is approximately 0.3 gpl Cu / v/o LIX-622 (see Table 8.73). Therefore, for the LIX-622 contents used in the design matrix a very large excess of reagent was present, e.g., even for the lowest concentration, 5 v/o LIX-622, the reagent has the ability to pick up approximately 1.5 gpl Cu from the aqueous solution (the starting solution contained only 0.66 gpl Cu). The data are important, however, to consider because they illustrate that even in the presence of a large excess of reagent that impurity pick-up by the organic is controllable, e.g., for the baseline condition lowering the pH of the aqueous phase from 1.25 to 1.0 should decrease the extraction of copper by only 0.5% but should decrease the extraction of all associated elements by 10% which would mean essentially no associated elements would be extracted (even in the presence of a large excess of reagent).

The above interpretation is confirmed in Table 8.74., where a high copper bearing solution (7.54 gpl Cu) is contacted with a 25 v/o LIX-622 organic phase, i.e., note that essentially no associated element is removed. The concentration of LIX-622 should have been slightly greater to more effectively remove all the copper.

The influence of pH on copper extraction from a sludge leach solution containing a high concentration of copper and iron is presented in Table 8.75.

Selective copper recovery from a mixed metal solution can be achieved from iron bearing solution (before jarosite) or from iron free solutions (after jarosite). However, the phase separations are not as fast or as clean for the before jarosite leach solutions.

TABLE 8.73. COPPER LOADING SUMMARY IN LIX 622 (25 v/o) - KERMAC 470B

Sample No.	gpl Cu / v/o LIX 622 @ pH = 1.75					
	O/A					
	10	5	2	1	0.5	0.2
1044	0.27					
1045		0.30				
1046			0.30			
1050			0.30			
1047				0.29		
1048					0.21	
1051					0.20	
1049						0.11

NOTE: ·See Table 8.57 for procedure.

·Maximum copper loading in organic phase: 14.4 gpl.

TABLE 8.74. LIX 622 ISOTHERM DATA: 25 v/o LIX 622 APPLIED TO JAROSITE TREATED SOLUTION

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Ni	Cr	Cd	Al
1042	Starting Solution (Barrel 2 sludge)	7.54	22.08	14.90	6.17	1.46	0.86	5.69
	Jarosite Solution							
1043	Unfiltered leach 1042 subjected to potassium jarosite conditions for 4 hours. Final pH = 1.75	7.69	6.53	15.43	6.60	1.24	0.94	4.72
	Isotherm (25 v/o LIX 622, 75 v/o KERMAC 470B							
	Organic exposed to solution 1043:							
1044	O/A = 10	0.10	6.56	15.56	6.64	1.25	0.95	4.77
1046	O/A = 2	0.17	6.71	16.01	6.87	1.28	0.97	4.86
1050	O/A = 2 (repeat)	0.23	6.58	15.62	6.67	1.26	0.95	4.79
1047	O/A = 1	0.53	6.68	15.93	6.87	1.28	0.97	4.88
1048	O/A = 0.5	2.33	6.68	16.56	6.99	1.31	1.00	5.02
1051	O/A = 0.5 (repeat)	2.68	6.56	15.61	6.66	1.25	0.94	4.78
1049	O/A = .2	4.81	6.50	15.30	6.53	1.23	0.92	4.70

TABLE 8.74. CONTINUED

NOTE: ·Standard leach on Barrel 2 sludge; 1/2 hr., 50^{o}C, pH = 1-1.5.

·Jarosite conditions: leach solutions plus leach solids subjected to conditions of: 90^{o}C, 4 hrs., K_2SO_4/Fe = 1, initial pH = 2.5.

·Organic phase: 25 v/o LIX 622, 75 v/o 470B contacted with 10 gpl Cu in ammonical solution for 3 min., then stripped with 180 gpl H_2SO_4.

·All contacts performed in 125 cc separatory vessels for 3 minutes at 20^{o}C.

TABLE 8.75. INFLUENCE OF PH ON COPPER EXTRACTION FROM SLUDGE LEACH SOLUTION: LIX 622

Solution pH (Initial)	Concentration in Solution After Contact (gpl)						
	Cu		Fe	Ni	Zn	Cr	Cd
	gpl	% Extracted					
1.00 (Feed-No Contact)	3.41	----	7.31	2.66	5.20	0.50	0.37
1.00	0.94	72.4	7.36	2.66	5.23	0.50	0.38
1.25	0.31	90.0	7.36	2.68	5.24	0.51	0.36
1.51	0.16	95.3	7.37	2.69	5.20	0.51	0.38
1.75	0.11	96.8	7.25	2.73	5.33	0.51	0.39
2.00	0.08	97.7	7.16	2.69	5.12	0.49	0.37

NOTE:
- ·10 v/o LIX-622
- ·90 v/o KERMAC 470B
- ·O/A = 1, 50 cc each, concentration corrected for dilution by pH adjustment
- ·One contact

8.6.2. Large Scale Copper Extraction Testwork

A large scale leach (1/10 design scale) was performed to supply leach solution (14 liters) for the new one-gallon mixer solvent extraction system. LIX-622 was used as the extractant. The results are presented in Table 8.76. Copper was removed from the leach solution to a level of 43 mg/liter. Other metal values were not extracted.

Results of large-scale testwork in the Reister SX system is presented in Table 8.77. Copper can be selectively and effectively removed from the leach solution. Phase separation is excellent and only after many hours of operation using the same reagent does a muck layer build up at the interface. The muck layer can be easily withdrawn by simple aspiration. The muck layer is fine particulate jarosite carried into the system in the leach solution.

The large scale testwork was probably not run sufficiently long to establish steady state conditions in the system. Henkel in their test work, even in a small continuous system, states(30) that they run tests for periods of at least 4-5 days to determine steady state conditions and to really understand what element distribution is occurring during the transfer and to understand if crud formation is going to be a problem. Long-term tests were performed during the Phase II study.

Several associated studies were performed to understand more about the control of the large scale SX system. One such study was to run the system near 500 cc/min. to determine if the interface levels could be established and maintained. The system was controllable and once the interface levels were established only minimum attention to adjustment was required. Chemical results from the control test are presented in Table 8.78.

At one point in the study it was felt that aging time of the leach solution may influence greatly the formation of crud and muck in the SX system. This supposition was proved unfounded (at least for aging times of one month). However, interesting small scale batch testwork was performed on aged solutions for copper extraction by LIX-622. Studies were conducted on leach solution (high iron) and jarosite treatment (low iron) leach solution. The influence of

TABLE 8.76. FIRST LARGE SYSTEM (ONE GALLON MIXER-SETTLER) TEST FOR COPPER EXTRACTION USING LIX 622

Conditions:
15 v/o LIX 622
85 v/o KERMAC 470B
Two Stages of Extraction
One Stage of Strip
pH of Leach Solution into System: 1.75
Temperature : 25^oC
Solution Flow Rate : 250 cc/minute
Total Volume Treated : 14 liters
Strip Acid : 200 gpl H_2SO_4

	Cu	Fe	Ni	Zn	Cr	Cd
Original Feed (gpl)	2.73	6.10	1.90	4.04	0.42	0.24
Raffinate (gpl)	0.043	6.14	1.94	4.12	0.42	0.25

TABLE 8.77. COPPER EXTRACTION BY LIX-622 DURING LARGE SCALE TESTWORK IN THE REISTER TESTRACK

Sample	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
	40 Liter Test (10 v/o LIX-622)							
1523	Starting Solution, pH = 2.14	1.37	0.65	4.94	0.28	3.02	0.31	0.55
1524	Raffinate (composite), pH = 1.73	0.017	0.68	5.14	0.29	3.18	0.33	0.56
	60 Liter Test (10 v/o LIX-622)							
1802	Starting Solution, pH = 1.9	0.39	1.13	8.89	0.26	8.02	0.41	0.44
1797	Raffinate, 1/2 hour	0.007	1.12	8.89	0.26	7.87	0.41	0.45
1805	" 2 hours	0.065	1.14	8.89	0.26	8.00	0.41	0.45
1816	" 4 hours	0.022	1.14	8.84	0.27	8.07	0.42	0.45
	90 Liter Test (10 v/o LIX-622)							
2127	Starting Solution, pH = 2.01	3.89	0.33	5.80	0.36	3.15	0.44	1.01
2129	Raffinate, 2 hours (pH = 1.38)	0.38	0.31	5.63	0.35	3.06	0.42	0.98
2142	" 6 hours	1.34	0.30	5.42	0.33	3.07	0.42	0.93
2144	" Composite	0.78	0.31	5.58	0.34	3.20	0.44	0.96
	160 Liter Test (15 v/o LIX-622)							
2494	Starting Solution, pH = 1.9	3.05	0.57	6.58	3.08	1.67	0.11	1.30
2499	Raffinate (composite) pH = 1.3	0.030	0.52	6.47	2.95	1.68	0.11	1.25

Continued

TABLE 8.77. CONTINUED

NOTES: ·Solutions treated for iron removal by jarosite precipitate prior to SX exposure.

·40 liter test conditions: 2-state extraction (O/A = 1)
1-stage strip (O/A = 1, 150 gpl H_2SO_4)
Flowrate: 250 cc/min. all phases
Temperature: 30-50^{o}C

·60 liter test conditions: 2-stage extraction (O/A = 1)
1-stage scrub (100 gpl K_2SO_4)
1-stage strip (O/A = 1, 175 gpl H_2SO_4
Flowrate: 250 cc/min. all phases
Temperature: 30-50^{o}C

·90 liter test conditions: 2-stage extraction (O/A = 1)
2-stage strip (O/A = 1, 150 gpl H_2SO_4
Flowrate: 250 cc/min. all phases
Temperature: 30-50^{o}C

·160 liter test conditions: 2-stage extraction (O/A = 1)
2-stage strip (O/A = 1, 175 gpl H_2SO_4)
Flowrate: 250 cc/min. all phases
Temperature: 30-50^{o}C

TABLE 8.78. CHEMICAL RESULTS ON LARGE SCALE Cu SX CONTROL TEST

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Ni	Cr	Zn	Cd	Al
2093	Feed (mixture of 1466 and 1991)	3.94	1.58	6.48	0.59	10.10	0.69	1.40
2092	Composite Raffinate (8 gallons - flow rate 250 cc/min.)	0.26	1.23	5.44	0.53	8.74	0.58	1.50
		(NOTE:	System at start-up contained 2 gal of previous leach solution ∴ can't compare decrease to 2093 feed)					
2094	Composite Raffinate (7 gallons - flowrate 475 cc/min.-design limit for system)	0.070	1.57	6.43	0.59	10.05	0.68	1.40
		(NOTE:	System switched from 250 cc/min. to 475 cc/min. so solution composition in cells same as feed 2093.					
2095	Strip from recycled above two tests	17.22	0.02	0.03	0.01	0.10	< D. L.	0.03

NOTE: ·10 v/o LIX 622, 90 v/o KERMAC 470B.

·Two stages of extraction (O/A = 1), two stages of strip (O/A = 1).

·System mixers each had a flowmeter installed and flows controlled at designed rates.

aging and solution dilution on LIX-622 extraction of copper was observed on each type of solution. The results for the non-jarosited solutions are presented in Table 8.79. The aging effect was very pronounced on undiluted leach, i.e., less copper was extracted from the longer aged solutions. There was not much difference between a five hour age (0.7 gpl Cu removed) and a 22 hour age (0.78 gpl Cu removed) but there was much more copper extracted from a 1.5 hour age (1.16 gpl Cu removed). The same trend was true of a 20 v/o diluted solution but essentially no aging effect was noted when the solution was diluted by 100 v/o.

The results for the jarosite treated leach solutions are presented in Table 8.80. The aging effect on undiluted leach solution showed 20 percent less pick-up of copper by a solution aged for 13 hours. There appears to be essentially no aging effect for the 20 v/o dilution and 100 v/o dilution test results.

Insufficient test work has been performed to establish the reason for the apparent aging effect in some cases and not in others. The effect may be of only academic interest because effective recovery has been found in the large scale continuous test work (at least for jarosite treated solutions) for solutions run without regard to storage time. Storage times ranged from a few hours to a few days.

8.6.3. Long Term Copper Extraction Testwork

A series of studies were conducted to investigate the stage and process efficiency and the possible degradation of the LIX-622 bearing organic phase. The system was described previously in Section 5.2.1. It consisted of three stages of extraction and two stages of sulfuric acid stripping.

The tests were conducted in the Bell Engineering solvent extraction testrack; 3.88 liters of 15 volume percent LIX-622 - 85 volume percent KERMAC 470B was contacted with 341 liters of aqueous leach solution over a period of 113 hours. Approximately 226 load/strip cycles were achieved. An aqueous/organic contact ratio of over 88 was achieved. The results of the

TABLE 8.79. INFLUENCE OF AGING TIME AND DILUTION ON LIX 622 EXTRACTION FROM LEACH SOLUTION

Sample No.	Condition	Concentration (gpl)								
		Cu	Fe	Ni	Zn	Cr	Cd	Al	Si	Ca
2054	Starting Leach Solution: Undiluted, pH = 1.5	1.25	12.01	5.19	5.69	0.66	0.40	1.85	1.37	0.60
2055	Repeat Analysis of 2054	1.24	11.84	5.13	5.62	0.65	0.40	1.84	1.36	0.59
2058	Leach Aged 1.5 hrs., then Contacted with LIX 622	0.085	11.67	5.10	5.58	0.65	0.39	1.82	1.34	0.58
2061	Leach Aged 3 hrs., then Contacted with LIX 622	0.320	12.21	5.32	5.78	0.67	0.41	1.88	1.39	0.61
6064	Leach Aged 5 hrs., then Contacted with LIX 622	0.531	12.25	5.31	5.80	0.67	0.41	1.88	1.40	0.61
2067	Leach Aged 22 hrs., then Contacted with LIX 622	0.464	12.42	5.43	5.93	0.69	0.42	1.91	1.42	.62
2056	Starting Leach Solution: 20 v/o Dilution, pH = 1.5	0.997	9.43	4.11	4.47	0.52	0.31	1.48	1.09	0.48
2059	Leach Aged 1.5 hrs., then Contacted with LIX 622	0.150	9.70	4.24	4.61	0.53	0.32	1.51	1.10	0.49
2062	Leach Aged 3 hrs., then Contacted with LIX 622	0.168	9.74	4.24	4.60	0.54	0.32	1.50	1.10	0.49
2065	Leach Aged 5 hrs., then Contacted with LIX 622	0.319	10.00	4.35	4.72	0.55	0.33	1.52	1.12	0.51

TABLE 8.79. CONTINUED

Sample No.	Condition	Concentration (gpl)								
		Cu	Fe	Ni	Zn	Cr	Cd	Al	Si	Ca
2091	Leach Aged 22 hrs., then Contacted with LIX 622	0.274	9.89	4.35	4.71	0.55	0.33	1.51	1.11	0.50
2057	Starting Leach Solution: 100 v/o Dilution	0.613	6.03	2.64	2.82	0.34	0.20	0.93	0.66	0.33
2060	Leach Aged 1.5 hrs., then Contacted with LIX 622	0.054	5.87	2.55	2.78	0.33	0.19	0.91	0.63	0.31
2063	Leach Aged 3 hrs., then Contacted with LIX 622	0.080	6.00	2.59	2.83	0.33	0.19	0.92	0.64	0.32
2066	Leach Aged 5 hrs., then Contacted with LIX 622	0.053	5.80	2.52	2.73	0.32	0.19	0.89	0.62	0.31
2069	Leach Aged 22 hrs., then Contacted with LIX 622	0.067	6.05	2.65	2.86	0.34	0.20	0.92	0.65	0.32

NOTE: ·Standard leach on barrel 18 material. Aging done in contact with leach solids.

·All Contacts made with 10 v/o LIX 622, 90 v/o KERMAC 470B, O/A = 1, T = 25°C, 3 minutes.

TABLE 8.80. INFLUENCE OF AGING TIME AND DILUTION ON LIX 622 EXTRACTION FROM JAROSITE LEACH SOLUTION

Sample No.	Condition	Concentration (gpl)								
		Cu	Fe	Ni	Zn	Cr	Cd	Al	Si	Ca
2077	Starting Leach Solution: Undiluted , pH = 1.8	0.71	0.68	5.55	6.50	0.35	0.45	1.41	1.53	0.65
2080	Leach Aged 1 hr., then Contacted with LIX 622	0.094	0.75	5.54	6.47	0.35	0.45	1.41	1.53	0.65
2083	3 hrs.	0.086	0.67	5.41	6.47	0.34	0.44	1.38	1.50	0.62
2086	13 hrs.	0.117	0.68	5.56	6.49	0.35	0.45	1.41	1.53	0.61
2078	Starting Leach: 20 v/o Dilution , pH = 1.8	0.562	0.58	4.38	5.13	0.28	0.35	1.11	1.20	0.53
2081	Leach Aged 1 hr., then contacted with LIX 622	0.049	0.61	4.33	5.11	0.28	0.35	1.10	1.18	0.52
2084	3 hrs.	0.042	0.58	4.36	5.09	0.28	0.35	1.10	1.17	0.52
2087	13 hrs.	0.064	0.59	4.43	5.14	0.28	0.36	1.12	1.20	0.53
2079	Starting Leach: 100 v/o Dilution, pH = 1.8	0.346	0.36	2.69	3.15	0.18	0.21	0.68	0.70	0.34
2085	Leach Aged 3 hrs., then Contacted with LIX 622	0.018	0.37	2.79	3.26	0.18	0.22	0.71	0.74	0.34
2088	13 hrs.	0.016	0.38	2.89	3.34	0.19	0.23	0.72	0.75	0.36

NOTE:
- Standard leach on barrel 18 material.
- Jarosite conditions: 6 hrs, initial pH = 2.2 , temp. = 90°C, $\frac{1\ g\ K_2SO_4}{1\ g\ Fe}$
- Aging done in contact with solids.
- All contacts made with 10 v/o LIX 622, 90 v/o KERMAC 470B, O/A = 1, T = 25°C, 3 minutes.

study are summarized in Table 8.81: stage efficiency and process rack efficiency in Table 8.82 and conditions for the testwork in Table 8.83. Complete experimental results are presented in Table 8.84. The results of degradation testwork performed on organic samples were presented previously in Tables 6.19 and 6.20.

Copper is effectively and selectively entrailed from a mixed metal solution (Table 8.81) by an organic phase that has been exposed to a large number of load/strip cycles. Degradation does not appear to be a problem over the test period studied. Stage efficiency for copper extraction from the aqueous phase (Table 8.82) decreases with number of stages. This is expected because the pH of the aqueous phase decreases as it moves from one stage to the next. The overall process efficiency for copper extraction is excellent and low copper bearing solutions are produced (Table 8.82).

The physical separation of phases in the settlers is rapid and without muck problems. A small amount of crud (solids) forms but it remains intact at the first interface and its source is most likely fine particulate solids carried over from the leach solid/liquid separation unit operation. The crud is easily removed by aspiration from the interface.

8.7. ZINC SOLVENT EXTRACTION (HIGH IRON FLOWSHEET)

A discussion was presented previously for a flowsheet to treat iron bearing solutions (a few grams per liter); Section 8.4. The discussion in this section relates to the high iron sludge treatment flowsheet that includes removal of most of the iron by a jarosite precipitation process; removal of copper by LIX-622 solvent extraction; then removal of zinc and residual iron (a few hundred mg/l). Therefore, the discussion of zinc extraction by SX is limited in this section to treatment of jarosite treated leach solutions.

A design matrix test series has been performed on a copper and iron free solution. The extraction results are presented in Table 8.85. (phase separation notes in Table 8.86). The solution used in this test series was exceptionally low in zinc content (1.24 gpl). Typical zinc contents of leach solutions are in the range of 3-5 gpl.

TABLE 8.81. LONG TERM DEGRADATION - EXTRACTION STUDY: COPPER BY 15 V/O LIX 622

Sample No.	Condition				Concentration in Final Composite Raffinate, gpl							
	Organic	Aqueous Exposure	Mixer Contact Time, (min.)		Cu	Fe	Zn	Cr	Ni	Al	Ca	P
		Hrs.	Feed	Strip								
		First Day										
3459	46.5	Starting Feed Solution			2.750	3.899	---	1.987	5.147	0.207	0.317	0.572
3475	46.5	15.5	279	186	0.054	3.727	0.111	1.940	5.750	0.217	0.318	0.570
		Second Day										
3482	40.0	Starting Feed Solution			3.130	4.068	0.131	2.084	6.260	0.248	0.331	0.656
3493	86.5	28.8	518.4	345.6	0.062	3.995	0.129	2.086	6.150	0.259	0.307	0.534
		Third Day										
3501-B	39.0	Starting Feed Solution			3.130	4.068	0.131	2.084	6.260	0.248	0.331	0.656
3509	125.5	41.8	752.4	501.6	0.106	3.958	0.122	2.060	6.291	0.281	0.344	0.607
		Fourth Day										
3519	36.0	Starting Feed Solution			3.332	3.809	0.127	2.030	5.749	---	---	0.652
3538-A	161.5	53.8	968.4	645.6	0.088	3.918	0.097	2.067	5.951	---	---	0.689
		Fifth Day										
3542	25.5	Starting Feed Solution			2.600	4.237	0.130	2.238	6.815	0.353	0.369	0.627
3547	187.0	62.8	1121.4	747.6	0.039	4.299	0.148	2.224	6.705	0.387	0.335	0.633

TABLE 8.81. CONTINUED

Sample No.	Condition				Concentration in Final Composite Raffinate, gpl							
	Organic Aqueous Exposure		Mixer Contact Time, (min.)		Cu	Fe	Zn	Cr	Ni	Al	Ca	P
	ℓ	Hrs.	Feed	Strip								
		Sixth Day										
3552	19.5	Starting Feed Solution			0.835	3.471	0.118	1.813	5.417	---	0.279	---
3567	206.5	68.8	1238.4	825.6	0.056	3.373	0.091	1.788	5.251	---	0.288	---
		Seventh Day										
3606	34.5	Starting Feed Solution			1.035	3.616	0.126	1.907	5.727	0.362	0.322	---
3613	241.0	79.3	1427.4	951.6	0.033	3.546	0.105	1.940	5.574	0.405	0.351	
		Eighth Day										
3619	34.5	Starting Feed Solution			2.045	3.117	0.099	1.725	5.019	0.354	0.303	---
3631	275.5	90.8	1634.4	1089.6	0.027	3.069	0.096	1.725	5.002	0.355	0.284	---
		Nintn Day										
3639	12.0	Starting Feed Solution			1.812	3.185	0.128	1.739	5.100	0.361	0.316	---
3643	287.5	94.8	1706.4	1137.6	0.073	3.125	0.121	1.959	5.652	0.406	0.348	---
		Tenth Day										
3651	27.0	Starting Feed Solution			2.026	2.746	0.079	1.515	4.464	0.318	0.356	---
3664	314.5	103.8	1868.4	1245.6	0.043	3.609	0.122	1.879	5.866	0.386	0.330	---

TABLE 8.81. CONTINUED

Sample No.	Condition				Concentration in Final Composite Raffinate, gpl							
	Organic Aqueous Exposure		Mixer Contact Time, (min.)		Cu	Fe	Zn	Cr	Ni	Al	Ca	P
	ℓ	Hrs.	Feed	Strip								
	Eleventh Day											
3670	27.0	Starting Feed Solution			2.225	3.078	0.105	1.693	5.046	0.373	0.276	---
3703	341.5	112.8 (226 Load/Strip Cycles)	2030.4	1353.6	0.049	3.126	0.112	1.687	5.071	0.383	0.277	---

NOTES: 'Conditions given for each day's testwork in Table 8.83.
'Total organic in extraction system = 2338 cc; in strip system 1550 cc.
'Total aqueous in extraction system = 2055 cc; in strip system 1370 cc.

TABLE 8.82. CELL EFFICIENCY FOR COPPER EXTRACTION BY LIX 622: LONG TERM TEST (Low Iron Flowsheet)

Sample No.	Conditions	Stage Efficiency, gpl in Raffinate, % Extracted						
		Cell 1		Cell 2		Cell 3		Total Efficiency
		gpl	%	gpl	%	gpl	%	
3459	Starting Solution 2.750 gpl (pH = 1.75)							
3463	6.0 Hrs. Continuous Exposure	0.216	92.1					
3464	" " " "			0.032	85.2			
3465	" " " "					0.018	43.8	99.3
3469	13.5 Hrs. Continuous Exposure	0.345	87.4					
3470	" " " "			0.038	89.0			
3471	" " " "					0.022	42.1	99.2
3482	Starting Solution 3.130 gpl (pH = 1.75)							
3486	21.5 Hrs. Continuous Exposure	0.867	72.0					
3487	" " " "			0.153	82.4			
3485	" " " "					0.053	65.4	98.3
3501-B	Starting Solution 2.697 (pH = 1.76)							
3504	34.8 Hrs. Continuous Exposure	0.483	82.1					
3505	" " " "			0.068	85.9			
3503	" " " "					0.072	----	97.3
3519	Starting Solution 2.700 (pH = 1.75)							
3526	47.8 Hrs. Continuous Exposure	0.734	72.8					
3527	" " " "			0.094	87.2			
3530	" " " "					0.097	----	96.4

TABLE 8.82. CONTINUED

Sample No.	Conditions	Stage Efficiency, gpl in Raffinate, % Extracted						
		Cell 1		Cell 2		Cell 3		Total Efficiency
		gpl	%	gpl	%	gpl	%	
3542	Starting Solution 2.600 (pH = 1.77)							
3544	57.8 Hrs. Continuous Exposure	0.233	83.8					
3545	" " " "			0.040	82.8			
3546	" " " "					0.040	0	98.5
3606	Starting Solution 1.035 (pH = 2.0)							
3608	73.8 Hrs. Continuous Exposure	0.027	97.4					
3609-A	" " " "			0.036	----			
3610-A	" " " "					0.026	27.8	97.5
3619	Starting Solution 2.045 (pH = 2.0)							
3632	84.3 Hrs. Continuous Exposure	0.142	93.1					
3633	" " " "			0.031	78.2			
3631	" " " "					0.027	12.9	98.7
3651-A	Starting Solution 2.026, (pH = 2.1)							
3658	99.8 Hrs. Continuous Exposure	0.593	76.7					
3659	" " " "			0.053	91.1			
3660-B	" " " "					0.015	71.7	99.4
3670	Starting Solution 2.225 gpl, (pH = 2.0)							

TABLE 8.82. CONTINUED

Sample No.	Conditions	Stage Efficiency, gpl in Raffinate, % Extracted						
		Cell 1		Cell 2		Cell 3		Total Efficiency
		gpl	%	gpl	%	gpl	%	
3700	112.8 Hrs. Continuous Exposure	1.116	49.8					
3701	" " " "			0.266	76.2			
3702	" " " "					0.068	77.4	96.9

NOTE: Detailed data presented in Table 8.81.

TABLE 8.83. CONDITIONS FOR TABLE 8.82 TESTWORK

Identifier Test Numbers	Description	Conditions			
		Initial Cu, gpl	Initial pH, R.T.	Volume Average, l	Temp.
3459, 3474	First Exposure of Organic	2.750	1.75	46.5	Feed 50°C Cell 1 35 Cell 2 30 Cell 3 27 Cell 4 24 Cell 5 24
3482, 3493	Second Exposure of Same Organic	3.130	1.75	40.0	
3501-B, 3509	Third " " " "	2.697	1.75	39.0	
3519, 3533	Fourth " " " "	2.700	1.75	39.0	
3542, 3548	Fifth " " " "	2.600	1.77	25.5	Feed 28°C
3552, 3567	Sixth " " " "	0.835	1.76	19.5	Feed 45°C
3606, 3613	Seventh " " " "	1.035	2.01	34.5	
3619, 3631	Eighth " " " "	2.045	2.01	34.5	Feed 44-55°C
3639, 3643	Ninth " " " "	1.812	2.13	12.0	Feed 50°C
3651, 3664	Tenth " " " "	2.026	2.14	27.0	Feed "
3670, 3703	Eleventh " " " "	2.225	2.01	27.0	Feed 25°C

TABLE 8.84. EXPERIMENTAL RESULTS FOR LONG TERM ORGANIC EXPOSURE TESTWORK: COPPER EXTRACTION WITH LIX 622

Sample No.	Conditions	Concentration in Final Composite Raffinate, gpl							
	First Day (46 l aqueous leach)	Fe	Cu	Zn	Cr	Ni	Al	Ca	P
3459	Starting Solution	3.899	2.750	0.102	1.987	5.847	0.207	0.317	0.572
3458	Starting Strip Acid, 200 gpl	---	32.22	0.004	0.002	---	---	---	---
	1.5 Hours								
3460	Cell 3	3.920	0.027	0.100	2.036	5.903	0.209	0.326	0.660
3461	Composite Raffinate	4.024	0.421	0.108	2.039	6.033	0.218	0.330	0.694
	3.0 Hours								
3462	Cell 3	4.120	0.025	0.090	2.124	6.135	0.224	0.332	0.696
	6.0 Hours								
3463	Cell 1	3.994	0.216	0.117	1.996	5.895	0.243	0.328	0.688
3464	Cell 2	3.758	0.032	0.112	1.927	5.755	0.230	0.315	0.604
3465	Cell 3	3.675	0.018	0.117	1.922	5.622	0.220	0.304	0.625
	7.5 Hours								
3466	Composite Raffinate	3.764	0.081	0.110	1.908	5.706	0.214	0.310	0.611
	13.5 Hours								
3469	Cell 1	3.899	0.345	0.102	1.959	5.781	0.223	0.318	0.580
3470	Cell 2	3.792	0.038	0.106	1.960	5.785	0.230	0.329	0.602
3471	Cell 3	3.859	0.022	0.113	2.002	5.957	0.240	0.322	0.631
3472	Composite Raffinate	3.866	0.024	0.112	1.971	5.891	0.225	0.321	0.677
3473	Strip Acid	0.034	34.5	---	---	---	---	---	---
	15.5 Hours								
3475	Final Composite	3.727	0.054	0.111	1.940	5.750	0.217	0.318	0.570

TABLE 8.84. CONTINUED

Sample No.	Conditions	Concentration in Final Composite Raffinate, gpl							
		Fe	Cu	Zn	Cr	Ni	Al	Ca	P
	Second Day (40 l aqueous leach)								
3482	Starting Solution	4.068	3.130	0.131	2.084	6.260	0.248	0.331	0.656
	5.0 Hours								
3484	Composite Raffinate	4.007	0.047	0.122	2.093	6.200	0.243	0.316	0.389
	6 Hours								
3486	Cell 1	3.877	0.867	0.125	1.989	5.995	0.245	0.316	0.760
3487	Cell 2	3.932	0.153	0.114	2.008	6.059	0.249	0.301	0.602
3488	Cell 3	3.901	0.076	0.126	2.002	5.956	0.244	0.301	0.660
	13.1 Hours								
3490	Cell 1	3.961	1.218	0.122	2.039	6.050	0.263	0.302	0.616
3491	Cell 2	4.180	0.227	0.105	2.171	6.394	---	0.308	0.645
3489	Cell 3	4.010	0.098	0.127	2.076	6.288	0.257	0.321	0.647
3493	Final Raffinate	3.995	0.062	0.129	2.086	6.150	0.259	0.307	0.534
3492	Strip Acid	0.052	42.56	---	---	---	---	---	---
	Third Day (39 l aqueous leach)								
3501-B	Starting Solution	4.033	2.697	0.120	2.014	6.057	0.242	0.324	0.700
	6 Hours								
3504	Cell 1	3.993	0.483	0.103	2.066	6.020	---	0.347	0.648
3505	Cell 2	3.916	0.068	0.112	2.018	6.143	0.293	0.353	0.623
3503	Cell 3	3.640	0.072	0.109	1.927	5.923	0.270	0.334	0.607

TABLE 8.84. CONTINUED

Sample No.	Conditions	Fe	Cu	Zn	Cr	Ni	Al	Ca	P
		Concentration in Final Composite Raffinate, gpl							
	7 Hours								
3506	Cell 3	3.851	0.078	0.114	1.986	6.043	0.265	0.335	0.605
	10 Hours								
3508	Cell 3	3.965	0.091	0.111	2.044	6.113	0.294	0.347	0.619
	13 Hours								
3510	Cell 1	3.925	1.072	0.130	2.059	6.095	0.290	0.361	0.716
3511	Cell 2	3.904	0.201	0.120	2.088	6.154	0.288	0.358	0.639
3509	Cell 3	3.958	0.106	0.122	2.060	6.291	0.281	0.344	0.607
3512	Strip Acid	0.052	36.03						
	Fourth Day (36 l aqueous leach)								
	3 Hours								
3525	Cell 3	3.786	0.041	0.112	2.029	6.042	0.283	0.319	0.667
	6 Hours								
3526	Cell 1	3.954	0.734	0.120	2.106	6.273	0.299	0.323	0.807
3527	Cell 2	3.987	0.094	0.115	2.093	6.342	0.309	0.331	0.771
3530	Cell 3	4.165	0.097	0.119	2.209	6.450	0.331	0.378	0.779
	12 Hours								
3531	Cell 1	4.140	0.910	0.131	2.127	6.494	0.305	0.370	0.777
3532	Cell 2	4.339	0.210	0.127	2.258	6.969	0.309	0.394	0.713
3533	Cell 3	---	---	---	---	---	---	---	
3538-A	Final Composite	3.918	0.088	0.097	2.067	5.951	---	---	0.689

TABLE 8.84. CONTINUED

Sample No.	Conditions	Concentration in Final Composite Raffinate, gpl Fe	Cu	Zn	Cr	Ni	Al	Ca	P
	Fifth Day (25 l aqueous leach)								
3542	Starting Solution	4.237	2.600	0.130	2.238	6.815	0.353	0.369	0.627
	3 Hours								
3543	Cell 3	4.247	0.048	0.127	2.228	6.810	0.378	0.367	0.678
	4 Hours								
3544	Cell 1	4.133	0.233	0.130	2.190	6.589	0.356	0.362	0.678
3545	Cell 2	4.103	0.040	0.137	2.185	6.752	0.357	0.362	0.533
3546	Cell 3	4.423	0.040	0.134	2.297	7.046	0.419	0.354	0.569
	8.5 Hours								
3547	Cell 3	4.299	0.039	0.148	2.224	6.705	0.387	0.335	0.633
3549	Strip Acid	0.078	41.08	---	---	---	---	---	---
	Sixth Day (20 l aqueous leach)								
3552	Starting Solution	3.471	0.834	0.118	1.813	5.417	---	0.279	---
	3 Hours								
3553	Cell 3	3.404	0.034	0.131	1.831	5.552	0.354	0.289	
	6.5 Hours								
3557	Cell 3	3.373	0.056	0.091	1.788	5.251	---	0.288	0.616

TABLE 8.84. CONTINUED

Sample No.	Conditions	Concentration in Final Composite Raffinate, gpl							
		Fe	Cu	Zn	Cr	Ni	Al	Ca	P
	Seventh Day (34 l aqueous leach)								
3606	Starting Solution	3.616	1.035	0.126	1.907	5.727	0.362	0.322	---
	3 Hours								
3607	Cell 3	3.609	0.029	0.126	1.952	5.918	0.319	0.337	---
	5 Hours								
3608	Cell 1	3.835	0.027	0.131	2.070	6.113	0.406	0.351	---
3609-A	Cell 2	3.681	0.036	0.120	1.992	5.817	0.426	0.365	---
3610-A	Cell 3	3.519	0.026	0.130	1.932	5.600	0.390	0.346	
	10.5 Hours								
3610-B	Cell 1	4.038	0.058	0.129	2.190	6.346	0.480	0.385	---
3611	Cell 2	3.857	0.016	0.119	2.093	6.142	0.447	0.368	---
3613	Final Composite	3.546	0.033	0.105	1.940	5.574	0.405	0.351	---
3614	Strip Acid	0.137	36.45	---	---	---	---	---	---
	Eighth Day (34 l aqueous leach)								
3619	Starting Solution	3.117	2.045	0.099	1.725	5.019	0.354	0.303	---
	3 Hours								
3620	Cell 3	3.067	0.039	0.114	1.717	4.982	0.361	0.314	---
	6 Hours								
3628	Cell 1	3.230	1.775	0.107	1.782	5.186	---	0.307	---
3629	Cell 2	3.152	0.030	0.101	1.731	5.003	0.351	0.296	

TABLE 8.84. CONTINUED

Sample No.	Conditions	Concentration in Final Composite Raffinate, gpl							
		Fe	Cu	Zn	Cr	Ni	Al	Ca	P
3627	Cell 3	3.193	0.036	0.111	5.785	5.146	0.356	0.297	---
	11.5 Hours								
3632	Cell 1	3.334	0.142	0.116	1.819	5.344	0.389	0.319	---
3633	Cell 2	3.165	0.031	0.110	1.735	5.033	0.359	0.294	---
3631	Cell 3	3.069	0.027	0.096	1.725	5.002	0.355	0.284	---
3634	Strip Acid	0.146	36.52	---	---	---	---	---	---
	Ninth Day (34 l aqueous leach)								
3639	Starting Solution	3.185	1.812	0.128	1.739	5.100	0.361	0.316	---
	4 Hours								
3640	Cell 1	3.494	0.387	0.126	1.874	5.458	0.398	0.345	---
3641	Cell 2	3.477	0.033	0.111	1.877	5.581	0.399	0.337	---
3642	Cell 3	3.443	0.013	0.019	1.845	5.392	0.381	0.335	---
	6 Hours								
3644	Cell 1	3.640	1.179	0.140	1.973	5.886	0.443	0.347	---
3645	Cell 2	3.670	0.361	0.127	1.999	5.936	0.409	0.345	---
3643	Cell 3	3.525	0.073	0.121	1.959	5.652	0.406	0.348	---
3646	Strip Acid	0.319	33.28						
	Tenth Day (27 l aqueous leach)								
3651	Starting Solution	2.746	2.026	0.079	1.515	4.464	0.318	0.356	---

TABLE 8.84. CONTINUED

Sample No.	Conditions	Fe	Cu	Zn	Cr	Ni	Al	Ca	P
		Concentration in Final Composite Raffinate, gpl							
	4 Hours								
3653	Cell 1	3.553	0.197	0.120	1.880	5.644	0.398	0.402	---
3654	Cell 2	3.196	0.023	0.109	1.731	5.006	0.362	0.402	---
3652	Cell 3	3.398	0.025	0.125	1.853	5.406	0.394	0.371	---
	6 Hours								
3656	Cell 1	3.396	0.181	0.114	1.802	5.379	0.384	0.382	---
3657	Cell 2	3.553	0.023	0.109	1.884	5.560	0.400	0.323	---
3655	Cell 3	3.305	0.019	0.109	1.772	5.336	0.368	0.401	---
	9 Hours								
3662	Cell 1	3.691	0.954	0.130	1.971	5.721	0.408	0.325	---
3663	Cell 2	3.682	0.136	0.131	1.961	5.883	0.405	0.328	---
3669	Cell 3	3.609	0.043	6.122	1.879	5.866	0.386	0.330	---
3669	Strip Acid	0.269	32.15						
	Eleventh Day (27 l aqueous leach)								
3670	Starting Solution	3.078	2.225	0.105	1.693	5.046	0.373	0.276	---
	3 Hours								
3672	Cell 1	3.035	1.037	0.088	1.642	4.869	0.347	0.269	---
3673	Cell 2	3.133	0.247	0.096	1.676	5.006	0.368	0.278	---
3674	Cell 3	2.956	0.046	0.100	1.638	4.859	0.344	0.277	---

TABLE B.84. CONTINUED

Sample No.	Conditions	Concentration in Final Composite Raffinate, gpl							
		Fe	Cu	Zn	Cr	Ni	Al	Ca	P
	6 Hours								
3677	Cell 1	3.024	1.116	0.094	1.645	4.814	0.369	0.276	---
3678	Cell 2	3.140	0.290	0.110	1.665	4.912	0.368	0.272	---
3679	Cell 3	3.017	0.054	0.097	1.640	4.874	0.353	0.260	---
	9 Hours								
3700	Cell 1	3.245	1.116	0.112	1.727	5.230	0.389	0.294	---
3701	Cell 2	3.064	0.266	0.098	1.682	5.006	0.379	0.277	---
3702	Cell 3	3.125	0.068	0.094	1.681	4.979	0.376	0.272	---
3703	Final Composite	3.126	0.049	0.112	1.687	5.071	0.382	0.277	---

NOTES: 'Test conditions in Table B.81 and Table B.83.

TABLE 8.85. DESIGN MATRIX FOR ZINC REMOVAL BY DEHPA FROM COPPER AND IRON FREE SOLUTION

Results: Extraction from Solution (%)

Sample		DEHPA (%)	Deconol (%)	Contact Time (min.)	Contact Temp. (°)	Solution pH		Zn	Cr	
	Base	20	10	3	40	1.95				
	Unit	5	10	2	15	0.25				
	High (+)	25	20	5	55	2.20				
	Low (-)	15	0	1	25	1.70				
	Test #							Zn	Cr	
552	1	-	-	-	-	-		68.5	8.4	
553	2	+	-	-	+	-		83.8	-1.6	
554	3	-	+	-	+	+		36.5	7.7	
555	4	+	+	-	-	+		57.4	16.1	
556-7	5	-	-	+	+	+		75.9(77.4)	15.1(11.2)	
558	6	+	-	+	-	+		86.2	11.0	
559	7	-	+	+	-	-		26.0	11.0	
560	8	+	+	+	+	-		37.0	-4.7	
561-2	Base							80.4(82.7	7.9 (7.3)	
Effects (%)										
Zn		7.2	-19.7	-2.6	-0.6	5.1				

NOTE: ·Initial solution composition (gpl):
1.24 Zn, 0.43 Cr, 1.91 Ni, 0.19 Cd,

·Kermac 470B make-up dilutent
·O/A = 1, 25 cc each
·Temp: 40°C

TABLE 8.86. OBSERVATION ON PHASE SEPARATION FOR DEHPA DESIGN MATRIX TEST (TABLE 8.64)

Test #	Observation
1	Very good phase separation, very little muck*
2	Very good phase separation, very little muck
3	Very good phase separation, very little muck
4	Very good phase separation, very little muck
5	Very good phase separation, little muck, very rapid
6	Very good phase separation, little muck, very rapid
7	Very good phase separation, little muck, very rapid
8	Very good phase separation, little muck
Base	Very good phase separation, no muck

*Muck = a layer of organic-aqueous that disappears slowly.

A series of preliminary shake tests to investigate zinc extraction from a jarosite treated leach solution was conducted, Table 8.87. The results are that zinc can be selectively extracted from a copper, iron free solution. Phase separation is very good for iron free solutions, but were very poor in the earlier work on zinc-iron solutions. The zinc extraction levels attained in the shake test were not very low because there was insufficient D_2EHPA present. Later experimental studies showed that about 0.15 gpl Zn is extracted by each one volume percent D_2EHPA; Table 8.88. Therefore, to totally remove the zinc from a 7.45 gpl solution would require 50 v/o D_2EHPA. Note that the data in Table 8.87. also shows that Deconol decreases zinc extraction (in agreement with the design matrix testwork reported in Table 8.85.). D_2EHPA isotherm data are presented in Table 8.89. These tests were performed with an organic phase deficit in sufficient quantity of D_2EHPA to completely remove the zinc. It also appears that some Ni, Cd, and Al are partially extracted. Extraction of Ni is not born out in large scale testwork. Aluminum and calcium (not shown in Table 8.89.) are co-extracted.

The shake testwork was followed by experimental work in the Bell Engineering 600cc continuous system. Results of a typical sequence test are presented in Table 8.90. The continuous testwork was run under D_2EHPA deficient conditions, i.e., according to data generated later in the study 0.15-0.17 gpl Zn are extracted per v/o D_2EHPA. Therefore, 40 v/o D_2EHPA should be able to maintain extraction of 6.0-6.8 gpl Zn. However, D_2EHPA also extracts ferric iron, some Al and Ca. Iron in the organic is not stripped so in a recycle system extraction sites are occupied and are unavailable for zinc extraction; also, Al that is extracted with the organic is only partially stripped by 200 gpl H_2SO_4. Calcium loaded into the organic phase precipitates when the organic phases cycles to the strip cells as gypsum. It can, however, be easily filtered from the aqueous phase and removed from the system. The data collected in the above testwork illustrates that long-term exposure of an organic phase to a leach solution is needed to establish the required bleed stream necessary to maintain an efficient regenerated D_2EHPA phase.

Large scale testwork in the Reister system supports this conclusion. The results of four major tests are presented in Table 8.91.

TABLE 8.87. DEHPA Solvent Extraction Applied to a Jarosite Treated Solution

Sample	Condition	Concentration (gpl)						
		Fe	Cu	Cr	Ni	Zn	Cd	Al
	Starting Solution							
1300	Solution after potassium jarosite precipitation (pH adjusted to 1.75)	0.33	4.51	0.38	2.07	6.91	0.30	3.68
	Copper Removal							
	Two contacts between solution and LIX 622 (20 v/o), O/A = 2, 3 min.	0.36	0.008	0.41	2.22	7.45	0.33	4.07
	DEHPA (40%, 60% 470B): 40°C							
1305	O/A = 1	0.044	0.005	0.41	2.23	1.46	0.32	2.86
1306	O/A = 2	0.036	0.005	0.44	2.40	1.19	0.33	2.52
1307	O/A = 2 (repeat)	0.033	0.005	0.44	2.40	1.19	0.33	2.22
	DEHPA (40%, 10% DEC, 50 v/o 470 B): 40°C							
1308	O/A = 1	0.048	0.005	0.41	2.26	3.39	0.33	2.83
1309	O/A = 2	0.039	0.005	0.43	2.39	1.82	0.33	2.80
1310	O/A = 2	0.033	0.005	0.41	2.28	1.69	0.31	2.42
	DEHPA (40 v/o, 60 v/o 470 B), H_2O_2 Oxidized, 40°C							
1311	O/A = 1	< D.L.	0.003	0.30	1.69	0.94	0.24	1.58
1312	O/A = 2	< D.L.	0.002	0.29	1.60	0.54	0.21	1.22
1313	O/A = 2 (repeat)	< D.L.	0.002	0.27	1.47	0.56	0.20	0.72
	DEHPA (40 v/o, 10% Deconol, 40% 470 B): H_2O_2 Oxidized							
1314	O/A = 1	0.000	0.002	0.29	1.60	1.46	0.22	1.26
1315	O/A = 2	0.001	0.003	0.30	1.67	1.01	0.21	1.57

TABLE 8.88. SUMMARY OF ZINC LOADING FOR 40 v/O DEHPA, 60 v/o KERMAC 470B

	gpl Zn/v/o DEHPA					
	10	5	2	1	0.5	0.2
PH = 2.0	0.19	----	----	0.15	----	0.10
pH = 2.5	0.17	0.17	0.17	0.15	0.13	0.09
pH = 3.0	0.18	----	----	0.12	----	0.09

NOTE: ·Max. organic loading approximately 18 gpl Zn.

·Organic solution pre-prepared by contacting with 100 gpl Zn solution, then stripping with 50 gpl Zn, 200 gpl H_2SO_4 (O/A = 1).

TABLE 8.89. DEHPA ISOTHERM DATA: 40 v/o DEHPA, 60 v/o KERMAC 470B

		Concentration (gpl)					
		Zn	Fe	Cu	Ni	Cd	Al
	PH = 2.0						
1926	Starting Solution	8.68	1.15	0.002	9.10	0.49	0.43
1928	O/A = 10						
	Aqueous	1.06	0.71	< D. L.	7.96	0.23	0.29
	Organic	0.76	0.04	----	0.11	0.02	0.01
1929	O/A = 1						
	Aqueous	2.63	0.95	< D. L.	8.91	0.43	0.34
	Organic	6.05	0.20	----	1.00	0.06	0.09
1930	O/A = 0.2						
	Aqueous	4.84	0.99	----	8.80	0.45	0.38
	Organic	18.80	0.30	----	----	----	0.40
	pH = 2.5						
1925	Starting Solution	8.46	1.13	0.002	9.14	0.48	0.42
1918	O/A = 10						
	Aqueous	1.57	6.73	0.010	8.78	0.24	0.30
	Organic	0.69	0.04	----	0.05	0.02	0.01
1919	O/A = 5						
	Aqueous	1.47	0.77	0.010	8.33	0.28	0.28
	Organic	1.40	0.07	----	0.16	0.04	0.03
1920	O/A = 2						
	Aqueous	1.78	0.94	< D. L.	9.08	0.40	0.32
	Organic	3.34	0.08	----	0.03	0.04	0.05

TABLE 8.89. CONTINUED

		Concentration (gpl)					
		Zn	Fe	Cu	Ni	Cd	Al
1924	O/A = 2 (Repeat of 1920)						
	Aqueous	1.60	0.85	< D. L.	8.25	0.36	0.29
	Organic	3.43	0.14	----	0.45	0.06	0.06
1921	O/A = 1						
	Aqueous	2.33	1.02	< D. L.	10.39	0.51	0.33
	Organic	6.12	0.11	----	----	0.03	0.09
1922	O/A = 0.5						
	Aqueous	3.11	0.93	< D. L.	8.34	0.42	0.35
	Organic	10.69	0.40	----	1.60	0.12	0.14
1923	O/A = .2						
	Aqueous	4.91	0.99	< D. L.	9.01	0.46	0.38
	Organic	17.72	0.70	----	0.65	0.10	0.20
	pH = 3.0						
1927	Starting Solution	8.33	1.12	0.002	9.07	0.47	0.42
1931	O/A = 10						
	Aqueous	0.94	0.67	< D. L.	8.45	0.22	0.27
	Organic	0.74	0.04	----	0.06	0.02	0.02
1932	O/A = 1						
	Aqueous	3.41	0.93	< D. L.	8.31	0.42	0.34
	Organic	4.92	0.09	----	0.76	0.05	0.08

TABLE 8.89. CONTINUED

		Zn	Fe	Cu	Ni	Cd	Al
1932	O/A = 1						
	Aqueous	3.41	0.93	< D. L.	8.31	0.42	0.34
	Organic	4.92	0.09	----	0.76	0.05	0.08
1933	0/A = 0.2						
	Aqueous	4.70	1.00	< D. L.	9.24	0.49	0.38
	Organic	18.15	0.60	----	----	----	----

NOTE: ·Organic pre-prepared by contacting with 100 gpl Zn solution, then stripping (O/A = 1) with 50 gpl Zn, 200 gpl H_2SO_4.

·Temperature: 25°C.

TABLE 8.90. DEHPA SOLVENT EXTRACTION OF ZINC: SMALL SCALE CONTINUOUS TEST

Sample	Conditions	Concentration (gpl)						
		Zn	Fe	Cr	Ni	Cd	Al	Ca
	Small SX System (600 cc mixer-settlers)							
2005	Starting Solution Initial pH = 2.0, aqueous phase pH readjusted to 2.0 after two extraction contacts	5.7	0.26	0.40	3.39	0.36	1.50	
2096	Raffinate from Stage Two after 3 hours	0.72	0.08	0.39	3.04	0.44	1.60	
2097	Raffinate from Stage Four after 3 hours	0.029	0.03	0.38	3.02	0.27	0.68	
2108	Raffinate from Stage Two after 7 hours	1.24	0.10	0.39	3.15	0.38	1.80	
2109	Raffinate from Stage Four after 7 hours	0.15	0.06	0.41	3.26	0.34	1.24	
2110	Strip after 7 hours of recycling (initially 200 gpl H_2SO_4)	33.05	<D.L.	0.01	0.11	0.18	0.84	

NOTES:
- 40 v/o DEHPA, 60 v/o KERMAC 470 B.
- Four stages of extraction, pH adjusted to 2.0 after first two contacts, O/A = 2, 50 cc/min. each phase flow rate, temp. 40-50°C.
- Three stages of strip, 200 gpl H_2SO_4 at start, strip recycled, O/A = 1, 50 cc/min. each phase, temp. 40-50°C.

TABLE 8.91. ZINC EXTRACTION BY DEHPA DURING TESTWORK IN THE REISTER TESTRACK

Sample	Condition	Concentration (gpl)						
		Zn	Fe	Cu	Cr	Ni	Cd	Al
	40 Liter Test (27 v/o DEHPA)							
1524	Starting Solution, pH = 1.75	5.14	0.68	0.017	0.29	3.18	0.33	0.56
1532	Raffinate, pH = 1.29	1.00	0.46	0.014	0.25	2.84	0.28	0.32
1533	Final Strip Solution	4.74	0.005	<D.L.	0.004	0.018	0.016	0.035
	60 Liter Test (40 v/o DEHPA)							
1811	Starting Solution, pH = 1.75	8.84	1.13	0.058	0.27	8.02	0.42	0.45
1814	Raffinate, 1.5 hrs.	1.79	0.97	0.050	0.27	8.06	0.40	0.27
1124	Raffinate, 3.25 hrs.	1.63	1.00	<D.L.	0.27	8.08	0.47	0.28
	Above raffinate adjusted to pH = 2.0 and recycled through system							
1826	pH Adjusted Feed	1.63	0.97	0.01	0.27	8.10	0.41	0.29
1827	Raffinate, 1 hour	0.09	0.60	----	0.26	7.99	0.29	0.06
1833	" 2.75 hours	0.58	0.60	----	0.27	8.67	0.37	0.06
	Above raffinate adjusted to pH = 2.5 and recycled through system (strip acid replaced with 200 gpl H_2SO_4)							
1882	Feed	0.58	0.60	----	0.27	8.67	0.37	0.06
1885	Raffinate, 1 hour	< D.L.	0.12	----	0.25	8.25	0.17	0.004
1889	" 3 hours	< D.L.	----	----	0.25	8.17	0.13	< D.L.

Continued

TABLE 8.91. (Continued)

Sample	Condition	Concentration (gpl)						
		Zn	Fe	Cu	Cr	Ni	Cd	Al
	90 Liter Test (40 v/o DEHPA)							
2177	Starting Solution, pH = 2.0	5.89	0.29	0.09	0.37	2.56	0.32	1.22
2178	Raffinate after second stage contact (see note below)	1.77	0.06	0.09	0.35	2.56	0.34	0.86
2179	Raffinate after fourth stage contact	0.15	0.02	0.08	0.34	2.44	0.22	0.53
2181	Final composite raffinate after fourth stage	0.13	0.01	0.08	0.37	2.54	0.24	0.49
2180B	Final composite strip	21.85	<D.L.	0.01	0.02	0.05	0.04	0.34
	Same system set-up as above, but different leach solution used (2092, jarosited, Cu SX prior treatment)							
2242	Starting Solution, pH = 3.0	4.94	0.58	0.11	0.26	2.69	0.27	0.81
2246	Raffinate after second stage contact, one hour	0.33	0.39	0.11	0.26	2.71	0.35	0.54
2246	Raffinate after fourth stage contact, one hour	0.04	0.19	0.10	0.28	2.72	0.27	0.34
2253	Raffinate after second stage contact, 3 hours	0.24	0.39	0.12	0.26	2.87	0.36	0.46
2256	Final composite raffinate	0.06	0.14	0.10	0.31	2.78	0.30	0.32
2255	Final Strip, 3 hours	42.83	<D.L.	0.04	0.01	0.07	0.19	0.91
	160 Liter Test (40 v/o DEHPA)							
2525	Starting Solution, pH = 2.0	6.20	0.37	0.04	2.79	1.77	0.14	1.20

Continued

TABLE 8.91. CONTINUED

.160 liter test conditions; 40 v/o DEHPA, 60 v/o KERMAC 470B
4-stage extraction (O/A = 1)
pH adjusted after first two contacts back to pH = 2
3-stage strip (O/A = 1), 200 gpl H_2SO_4
Flowrate: 250 cc/min. all phases
Temperature: 30-40°C

8.8. SOLVENT REAGENT DEGRADATION TESTWORK

8.8.1. Copper Solvent Extraction: LIX-622

8.8.1.1. Continuous Testwork

A series of tests were performed to investigate potential reagent degradations. A large number of load/strip cycles were performed in the Bell Engineering testrack over a period of 11 days. The extraction results and a summary of the degradation results were reported previously in Sections 8.6.3 and 6.3.4.

A small amount of organic (3.88 l of 15 v/o LIX-622) was exposed to a large amount of aqueous solution (>340 l) in a series of three extraction cells and two strip cells. The smaller Bell system was chosen over the larger Reister system so that less leach solution was required. The Reister system (5 cells) held 18.5 liters of organic (at an O/A = 1 loading). The amount of aqueous leach solution that could be contacted with the organic in one eight-hour day was 192 liters. Therefore, the largest possible aqueous/organic contact ratio achievable per day was 10.4. The same aqueous/organic ratio in the Bell system required 40 liters of aqueous solution. Therefore, the 340 liters of (aqueous solution) of contact achieved in the Bell system would have required 3540 liters of aqueous solution in the Reister system. A decision was, therefore, made to conduct the long-term multiple load/strip testwork in the Bell system.

The California sludge contained primarily chromium and nickel. The sludge was leached, then doped with copper, iron, and zinc.

The contact system was described previously, Section 5.2.1. It consisted of three stages of extraction (loading) and two stages of strip. The organic/aqueous ratio was one in all cells. Solution pH was adjusted before entering the first cell but was unadjusted thereafter. Phase mixing and settling times were both (in all cells) approximately seven minutes at a flowrate of 50 cc/min.

The organic was 15 v/o LIX-622, 85 v/o KERMAC 470B. The system cells and pump reservoir were loaded with 3.88 liters of organic, 1.8 liters of leach solution (cells 1,2,3) and 1.2 liters (cells 4,5) of strip acid (200 gpl H_2SO_4). The strip cells were fed from a four liter reservoir. The acid contact was maintained at 200 gpl by systematic replacement of acid as required.

The system was started up, flows and interfaces established and sampling of each raffinate was conducted periodically. The system was run under specified conditions of copper content, solution pH and temperature. Crud formation (if any) and phase disengagement was observed and noted. The test period continued until a desired volume of aqueous was run through the system; then shut down overnight. The next run was initiated the next day using a new feed solution. The leach solution in the system from the prior day's contact was unchanged. Interfaces were already established and it was found that system restart involved no more than calibrating flow rates and turning on the agitator and pump motors.

The extraction results for the eleven day test period were presented in Table 8.84. Extraction of copper was excellent and selective. Crud formation was unimportant and the small amount that did form was most likely fine particulate material from the filter unit operation. It was easily removed by aspiration.

8.8.1.2. Degradation Results

Degradation was followed by: the ability of the system to maintain low copper content in the final raffinate; and by a special test procedure performed on samples of organic collected at the end of each day's test. Neither of these tests showed degradation to be occurring. The results for the system final raffinate are presented in Tables 6.19, 6.20, 8.81 and 8.84.

The degradation test performed on the periodic organic samples consisted of: stripping the organic twice with unused 200 gpl H_2SO_4 acid; contacting the stripped organic with a stock mixed metal leach solution containing 3.11 gpl Cu (O/A = 1); then recontacting the leach solution with another sample of stripped system organic (O/A = 1); and measuring the effect of the two contacts on the copper (and other metal) content by ICP analysis. The results are presented in Tables 6.19 and 6.20. These tables are reproduced here as a convenience to the reader (8.92, 8.93).

Degradation of extractant for the conditions tested does not appear to be important. Approximately three liters (3.88) of organic was contacted with over 340 liters of aqueous leach solution over a period of 113 hours. This contact involved approximately 226 load/strip cycles; 678 mixer contacts of loading and 452 mixer contacts of stripping. An aqueous to organic contact ratio of 88 was achieved for the test period; an aqueous to LIX-622 reagent contact ratio of 587 was achieved for the test period.

Further, long term continuous testwork may be desirable but significant deterioration by the solution conditions of high metal content, high ionic strength, the presence of phosphorus, low pH, and mild temperature (40-50°C) does not appear to occur. It would be desirable to conduct a detailed analysis on the organic phase to determine if degradation of the LIX-622 oxime could be followed directly. This laboratory was not capable of performing such analyses and, therefore, an indirect approach was chosen.

8.8.2. Iron, Zinc Solvent Extraction: D_2EHPA

8.8.2.1. Continuous Testwork

A series of tests were performed to investigate potential reagent degradation. A large number of load/strip cycles were performed in the Bell Engineering testrack over a period of eight days. The extraction results were reported previously in Section 8.4.2.

A small amount of organic (7.6 liters of D_2EHPA) was exposed to a large volume of aqueous solution (150 l) in a series of four extraction cells and six strip cells; four sulfuric, three hydrochloric (Figure 8.20). The Bell system was chosen over the larger Reister system so that less leach solution was required. The Reister system (10 cells) held 37 liters of organic (at an O/A = 1 loading). The amount of aqueous leach solution that could be contacted with

TABLE 8.92. LIX 622 LONG TERM EXPOSURE DEGRADATION TEST SUMMARY

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Copper Concentration in Aqueous Phase (gpl)	
			System Organic	New Organic
	Starting Aqueous Solution, 3.112 gpl Cu			
	First Day			
3478	46.5 liters	First	0.061	
3479	" "	Second	0.008	
3480	None	First		0.121
3481	"	Second		0.006
	Second Day			
3495	86.5 liters	First	0.103	
3496	" "	Second	0.027	
3497	None	First		0.031
3498	"	Second		0.000
	Third Day			
3514	125.5 liters	First	0.114	
3515	"	Second	0.016	
3516	None	First		0.035
3517	"	Second		0.016
	Fourth Day			
3536	161.5 liters	First	0.109	
3537	" "	Second	0.019	
3540	None	First		0.028
3541	"	Second		0.001

CONTINUED

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Copper Concentration in Aqueous Phase (gpl)	
			System Organic	New Organic
	Fifth Day			
3550	187.0 liters	First	0.001	
3551	None	First		0.040
	Sixth Day			
3615	206.5 liters	First	0.036	
3616	" "	Second	0.008	
3617	None	First		0.006
3618	"	Second		0.007
	Seventh Day			
3635	241.0 liters	First	0.112	
3636	" "	Second	0.022	
3637	None	First		0.024
3638	"	Second		0.007
	Eighth Day			
3647	275.5 liters	First	0.258	
3648	" "	Second	0.023	
3649	None	First		0.053
3650	"	Second		0.004
	Ninth Day			
3665	287.5 liters	First	0.120	
3666	" "	Second	0.000	
3667	None	First		0.015
3668	"	Second		0.020

CONTINUED

Notes:
- Conditions for each days exposure given in Table 8.82.
- Degradation test conditions: 50cc system organic stripped twice (O/A =1) with unused 200 gpl H_2SO_4; stripped organic contacted with copper stock solution, pH = 1.36 for first four tests, pH = 2.0 for last five tests; a second system organic sample contacted same stock solution, i.e., stock solution was contacted twice with two used organic samples, stock pH not adjusted between contacts.

Unused organic same as system organic, 15 % LIX 622, contacted with a 30 gpl Cu, 200 gpl H_2SO_4 solution, then contacted with stock solution as described above for system organic.

TABLE 8.93. LIX 622 LONG TERM EXPOSURE DEGRADATION TEST SUMMARY: LOADING.

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Loading, gpl/% LIX 622	
			System Organic	New Organic
	Stock Aqueous Solution, 3.112 gpl Cu, 3.958 gpl Fe, 0.122 gpl Zn, 2.014 gpl Cr, 6.061 gpl Ni, 0.287 gpl Al, 0.319 gpl Ca			
	First Day			
3478	46.5 liters Aqueous	First	0.203	
3479	" "	Second	0.004	
3480	None	First		0.199
3481	"	Second		0.008
	Second Day			
3495	86.5 liters	First	0.200	
3496	" "	Second	0.005	
3497	None	First		0.205
3496	"	Second		0.014
	Third Day			
3514	125.5 liters	First	0.200	
3515	"	Second	0.006	
3516	None	First		0.205
3517	"	Second		0.001
	Fourth Day			
3536	161.5 liters	First	0.200	
3537	"	Second	0.006	
3540	None	First		0.206
3541	"	Second		0.002

CONTINUED

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Loading, gpl/% LIX 622	
			System Organic	New Organic
	Fifth Day			
3550	187.0 liters	First	0.207	
3551	None	First		0.205
	Sixth Day			
3615	206.5	First	0.205	
3616	"	Second	0.002	
3617	None	First		0.207
3618	"	Second		-
	Seventh Day			
3635	241.0 liters	First	0.200	
3636	"	Second	0.006	
3637	None	First		0.206
3638	"	Second		0.001
	Eighth Day			
3647	275.5 liters	First	0.190	
3648	"	Second	0.016	
3649	None	First		0.204
3650	"	Second		0.003
	Ninth Day			
3665	287.5 liters	First	0.199	
3666	"	Second	>0.013	
3667	None	First		0.206
3668	"	Second		-

Note: . Conditions for each days exposure presented in Table 8.83.

the organic in one eight-hour day was 192 liters. Therefore, the largest possible aqueous/organic contact ratio achievable per day was 5.2. The same aqueous/organic ratio in the Bell system required 40 liters of aqueous solution. Therefore, the 150 liters (of aqueous solution) of contact achieved in the Bell system would have required 780 liters of aqueous solution in the Reister system. A decision was, therefore, made to conduct the long-term multiple load/strip testwork in the Bell system.

The contact system is shown schematically in Figure 8.20. It consisted of one stage of low pH contact for high iron removal from the leach solution; and three stages of iron and zinc extraction; one stage of zinc stripping (by sulfuric acid) from the iron loaded organic followed by three stages of iron stripping by hydrochloric acid; and two additional stages of zinc stripping by sulfuric acid. The organic/aqueous ratio was one in all cells. Solution pH was adjusted to approximately one before entering the first cell, then readjusted to approximately two before entering the second cell. The solution pH was unadjusted thereafter. Phase mixing and settling times were both (in all cells) approximately seven minutes at a flowrate of 50 cc/min.

The organic was 40 v/o D_2EHPA, 60 v/o KERMAC 510. The system cells and pump reservoir was loaded with 7.6 liters of organic; 1.8 liters of leach solution (cells 1,2,3,4); 2.4 liters of sulfuric strip acid (200 gpl H_2SO_4, cells 5,6,7); and 2.4 liters of hydrochloric strip acid (6 N HCl, cells 8,9,10). The acid contents of the strip cells were maintained at their desired strength by systematic replacement of acid as required.

The system was started up, flows and interfaces established and sampling of each raffinate was conducted periodically. The system was run under specified conditions of zinc content, solution pH and temperature. Crud formation and phase disengagement was observed and noted. The test period continued until a desired volume of aqueous was run throug the system; then shut down overnight. The next run was initiated the next day using a new feed solution. The leach solution in the system from the prior day's contact was unchanged. Interfaces were already established and it was found that system restart involved simply calibrating pump flows and turning on the agitator and pump motors.

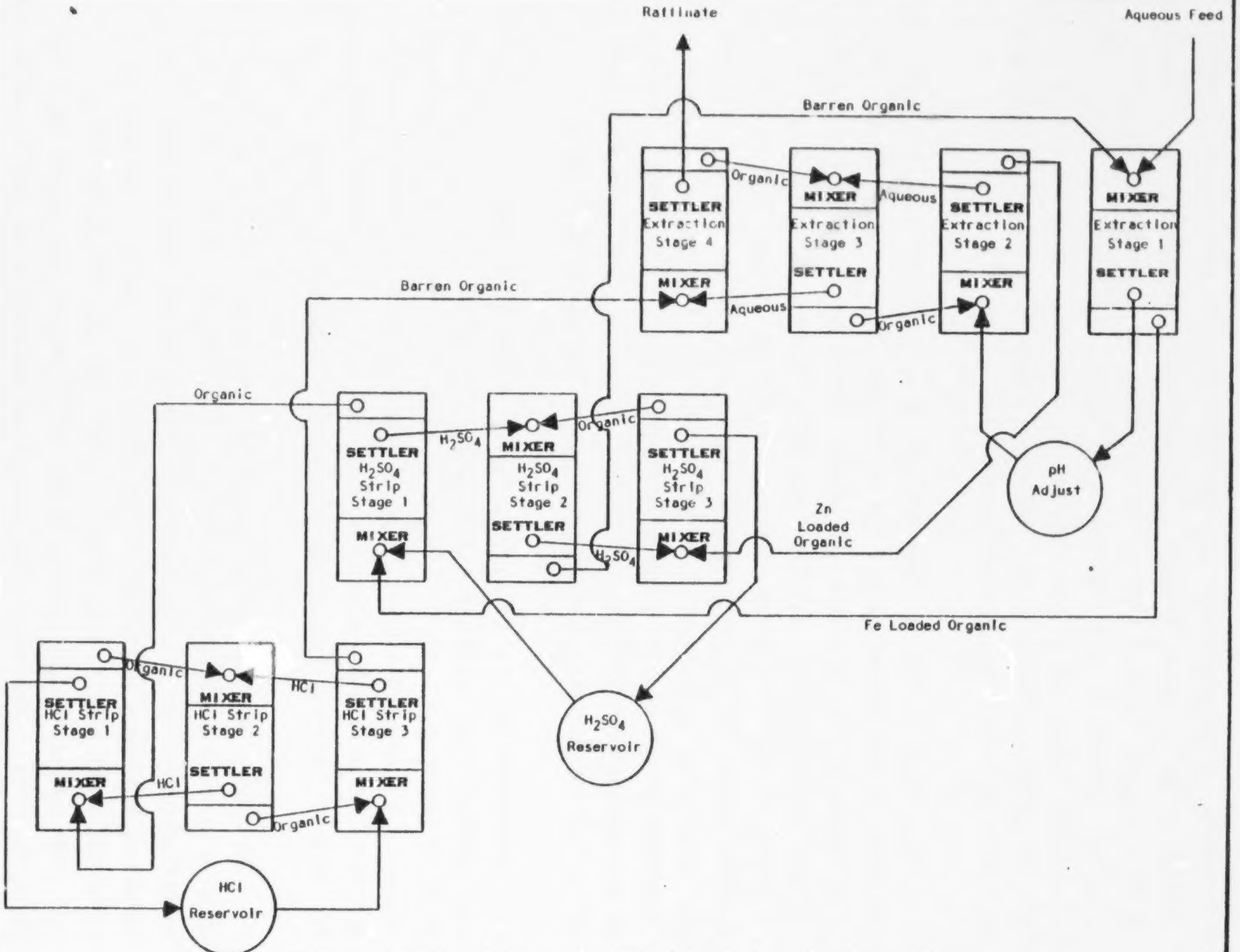

Raffinate
Aqueous Feed
Barren Organic
Organic
MIXER
Aqueous
SETTLER
Extraction
Stage 4
Extraction
Stage 3
Extraction
Stage 2
Extraction
Stage 1
Barren Organic
Aqueous
Organic
Organic
H$_2$SO$_4$
Organic
SETTLER
H$_2$SO$_4$
Strip
Stage 1
MIXER
H$_2$SO$_4$
Strip
Stage 2
SETTLER
H$_2$SO$_4$
Strip
Stage 3
H$_2$SO$_4$
pH
Adjust
Zn
Loaded
Organic
Fe Loaded Organic
Organic
HCl
SETTLER
HCl Strip
Stage 1
HCl Strip
Stage 2
HCl Strip
Stage 3
HCl
Organic
H$_2$SO$_4$
Reservoir
HCl
Reservoir

Figure 8.20. Schematic of iron, zinc long term test system flow pattern.

The extraction results for the eight-day test period were presented in Table 8.53. Extraction of iron and zinc were excellent. Crud formation in the first cell was a problem (see Section 8.4.3) until the system diluent was switched to KERMAC 510 kerosene.

8.8.2.2. Degradation Results

Degradation was followed by: the ability of the system to maintain low iron and zinc concentrations in the final raffinate; and by a special test procedure performed on samples of organic collected at the end of each day's test. Neither of these tests showed degradation to be occurring. The results for the system final raffinates are presented in Table 8.53.

The degradation test performed on the periodic organic samples consisted of: stripping the organic twice with unused 200 gpl H_2SO_4 acid; contacting the stripped organic with a stock mixed metal solution containing more iron and zinc than a 40 v/o D_2EHPA organic could extract containing 11.64 gpl Fe, 11.19 gpl Zn (O/A = 1); then recontacting the leach solution with another sample of stripped system organic (O/A = 1); and measuring the effect of the two contacts on the zinc and iron (and other metals) content by ICP analysis. The results were presented previously in Table 6.24 and are reproduced here as a convenience to the reader (8.94).

Degradation of extractant for the conditions tested does not appear to be important. Approximately 7.6 liters of 40 volume percent D_2EHPA-60 in KERMAC 510 kerosene was contacted with over 150 liters of aqueous leach solution over a period of 67 hours. This contact involved approximately 58 load/strip cycles; 232 mixer contacts of loading and 586 mixer contacts of stripping. An aqueous to organic contact ratio of 20 was achieved for the test period. An aqueous to D_2EHPA reagent contact ratio of 50 was achieved for the test period.

Degradation test results are presented in Table 8.95. No noticeable decrease in the ability of the reagent to effectively extract iron and zinc is shown over the test period considered. It would be desirable to conduct a detailed analysis on the organic phase to determine if degradation of the

TABLE 8.94. DEHPA LONG TERM EXPOSURE DEGRADATION TEST

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Loading, gpl (Zn+Fe)/% DEHPA	
			System Organic	New Organic
4025	Stock Aqueous Solution, pH = 2.0, 11.639 gpl Fe, 11.192 gpl Zn			
	First Day			
3841	19 liters aqueous	First	0.257	
3842	" "	Second	0.068	
3843	None	First		0.327
3844	"	Second		0.032
	Second Day			
3874	38 liters	First	0.261	
3875	" "	Second	0.054	
3876	None	First		0.270
3877	"	Second		0.056
	Third Day			
3909	57 liters	First	0.242	
3910	" "	Second	0.066	
3911	None	First		0.286
3912	"	Second		0.051
	Fourth Day			
3947	76 liters	First	0.271	
3948	" "	Second	0.056	

CONTINUED

Sample No.	Organic Exposure To Aqueous Phase	Contacts	Loading, gpl (Zn+Fe)/% DEHPA	
			System Organic	New Organic
3947	None	First		0.259
3948	"	Second		0.068
	Fifth Day			
3982	96 liters	First	0.248	
3983	" "	Second	0.054	
3984	None	First		-
3985	"	Second		-
	Sixth Day			
4026	115 liters	First	0.286	
4027	" "	Second	0.029	
4028	None	First		0.278
4029	"	Second		0.065

Notes: . Detailed experimental results presented in Table 8.95.

TABLE B.95 LONG-TERM DEGRADATION-EXTRACTION STUDY: ZINC AND IRON BY 40% DEHPA

Sample No.	Conditions					Concentration in Final Cell 4 Composite Raffinate, gpl	
	Aqueous Exposure to Organic		*Mixer Contact Time, min.				
	ℓ	Hrs.	Feed	Strip		Fe	Zn
				H_2SO_4	HCl		
	First Day						
3798	19	14	336	252	252	0.342 (high because of incomplete iron oxidation)	0.005
	Second Day						
3835	38	23	552	414	414	0.070	0.094
	Third Day						
3871	57	29.5	708	531	531	0.030	0.106
	Fourth Day						
3908	76	37.5	900	675	675	0.319 (high because of incomplete iron oxidation)	0.046
	Fifth Day						
3944	96	44.5	1068	800	800	0.027	0.031

CONTINUED

Sample No.	Conditions					Concentration in Final Cell 4 Composite Raffinate, gpl	
	Aqueous Exposure to Organic		*Mixer Contact Time, min.				
		Hrs.	Feed	Strip		Fe	Zn
				H_2SO_4	HCl		
	Sixth Day						
3975	115	51.5	1236	927	927	0.238 (high because of incomplete oxidation)	0.046
	Seventh Day						
4022	133	59	1416	1062	1062	0.051	0.066
	Eighth Day						
4054	151	67	1608	2010	2010	0.028	0.043

NOTES: ˙Conditions for each day's exposure presented in Table 8.83.

˙Mixer contact time is time organic was exposed to feed solution or to strip solution.

D_2EHPA reagent (or if decomposition products could be identified) could be followed directly. This laboratory was not capable of performing such analyses and, therefore, an indirect approach was chosen.

8.9. CHROMIUM OXIDATION

Selective removal of Cr^{+3} ions from a mixed metal solution containing Cu^{+2}, $Fe^{+2,+3}$, Zn^{+2}, Ni^{+2}, and Al^{+3}, does not appear possible without conversion to an oxidized, CrO_4^{-2} or $Cr_2O_7^{-2}$, form. Conversion to chromate or dichromate requires a strongly oxidizing environment which means that the oxidation must be accomplished after solvent extraction processes because a strongly oxidizing solution is expected to degrade the organic extraction reagents. The proper place for the chromium oxidation unit operation, therefore, appears to be after Fe, Cu, and Zn have been removed.

There does not appear to be a successful way of selectively separating Cr^{+3} from mixed metal solutions by SX. Reagents that have been successful in extracting Cr^{+3} from an aqueous phase suffer from slow strip kinetics when using H_2SO_4 acid or require that HCl be the stripping agent. Certainly consideration of Cr^{+3} removal by SX techniques is in the laboratory stage of investigation rather than in industrial practice. Known studies on Cr^{+3} SX are listed in Reference 40.

Two approaches to chromium oxidation are proposed, i.e., 1) solution oxidation or 2) sludge oxidation by roasting. Each approach has several alternate means available to accomplish the oxidation.

8.9.1. Solution Oxidation of Chromium

Emphasis was placed in this study on solution oxidation techniques for chromium. The experimental technique used to determine the degree of oxidation was: expose a known volume of solution to a set of oxidizing conditions; separate solids if present; treat a known volume of the solution to ion exchange using the anion exchanger IRA 900 (this quantitatively removes all anion species formed during the oxidation, i.e., $CrO_4^{=}$, $Cr_2O_7^{=}$, or $HCrO_4^{-}$); releach any solid phase to complete the mass balance.

Studies have been conducted using H_2O_2, PbO_2, Na_2O_2, Cl_2, and aqueous chloride ion containing species such as HClO. The emphasis was placed on Cl_2 as the oxidizing agent became of its ability to easily raise the solution Eh to above the Cr^{+3}/CrO_4^{-2} (or $Cr_2O_7^{-2}$) equilibrium half cell potential.

8.9.1.1. Chlorine Oxidation of Chromium

8.9.1.1.1. Phase I Studies

Small scale testwork was conducted on: chromium solutions made in the laboratory; chromium bearing leach solutions pretreated in a variety of ways; and chromium bearing leach solutions produced in the large test assembly. The experimental results are presented in Tables 8.96-8.98.

All testwork was performed on leach solutions that had been pretreated for removal of most of the iron, copper, and zinc, i.e., a leach solution was oxidized that contained primarily chromium and nickel. Preliminary testwork showed that oxidation rates were significantly more rapid in slurry bearing solutions ($4<pH<6$) than in acid solutions (pH 2), i.e., oxidation of chromium from a precipitated hydroxide was more rapid than oxidation of chromium in solution. These results are illustrated in Tables 8.96 and 8.98.

Three experimental approaches were taken: chlorine was sparged continuously into the chromium bearing solution (Table 8.96), pH was maintained at a specified value; chlorine was sparged periodically into the solution to maintain the Eh > 1000 mv, and pH was maintained at a specified value (Table 8.97); or chlorine was sparged into a pH adjusted (pH = 5) solution, without maintaining the pH, until all solids were dissolved, then the cycle repeated (Table 8.98).

The results presented in Table 8.96 show a comparison of the chromium oxidation achieved in three types of leach solutions. The chromium oxidation in a specific time period is less in unpretreated leach solutions (containing Cu, Fe, Zn, Cr, Ni, Cd, and Al) than in jarosite treated (Fe removed) and jarosite-CuSX-ZnSX (Fe, Cu, Zn removed) treated solutions.

TABLE 9.96. CHLORINE OXIDATION OF CHROMIUM AS A FUNCTION OF PH AND TYPE STARTING SOLUTION

Sample No.	Condition	Chromium Oxidized (%)
1964	Leach Solution (2.44gpl Cr^{+3})	
2009	pH = 2.2	58.3
1979	pH = 4.0	59.7
	pH = 5.0	63.8
1988	Jarosite Treated Leach Solution (5.80gpl Cr^{+3})	
2011	pH = 2.1	60.0
2027	pH = 4.0	85.8
2033	pH = 5.0	84.9
2038	Jarosite - Cu SX - Zn SX Treated Leach Solution (4.46gpl Cr^{+3})	
2051	pH = 1.8	47.5
2040	pH = 4.0	85.9
2046	pH = 5.0	83.3

Notes:

- All oxidation tests performed on 100 cc of pH adjusted leach solution; pH maintained; 0.2 liters Cl_2/ min.; contact time one hour.
- Analytical procedure: solution contact performed; sample filtered; solution analyzed; solution contacted with IRA 900 for chromate removal; solution from IX analyzed; solids leached; all solution volumes recorded; oxidation calculated from mass balance.
- Starting solutions prepared by standard leach of barrel 12 sludge. The starting solution concentrations (gpl) were:

	Cr	Ni	Al	Fe	Cu	Zn	Cd
1964	2.44	4.55	1.52	8.32	0.73	2.91	0.23
1988	5.80	5.60	1.66	0.73	0.84	2.99	0.37
2038	4.46	3.91	0.74	0.03	0.02	0.29	0.24

TABLE 9.97. CHLORINE OXIDATION OF CHROMIUM: Eh MAINTAINED

Sample No.	Condition	Chromium Oxidized (%)
2190	Starting Solution (3.00gpl Cr^{+3}) pH = 1.4, Eh = 374mv	
	pH = 1.4	
2200	Fifteen minute exposure, 1160mv	8.6
2206	One hour exposure, 1140mv	7.0
	pH = 5.0	
2234	One-half hour exposure, 1138mv	81.0
2237	one hour exposure, 1136mv	84.6
2181	Starting Solution (0.37gpl Cr^{+3}) pH = 1.5, Eh = 191mv	
	pH = 1.5	
2197	one hour exposure, 1135mv	10.3
	pH = 4.0	
2212	One-half hour exposure, 1088mv	30.5
2215	One hour exposure, 1102mv	45.8
	pH = 5.0	
2223	One-half exposure, 1088mv	54.8
2226	One hour exposure, 1099mv	72.7

Notes:
- Starting Solution Composition (gpl):

	Cr	Ni	Al	Fe	Cu	Zn	Cd
2190	3.00	2.39	0.46	0.01	0.08	0.12	0.23
2181	0.37	2.54	0.49	0.01	0.08	0.13	0.24

- 500cc solution from sequential test series four. Solution treated previously for iron, copper and zinc removal. Series 2190 was doped with chromium.
- Chlorine addition rate 0.2 l/min but only supplied periodically to keep the solution Eh >1000mv. PH maintained.

TABLE 9.98. CHLORINE OXIDATION OF CHROMIUM: CYCLE TEST

Sample No.	Condition	Chromium Oxidized (%)
2417	Starting Solution (2.47gpl) pH = 1.43, Eh = 373mv	
2418	pH adjusted to 5.0, chlorine purged at 0.2 l/min until all solids dissolved, Eh= 1000mv, 25 min., 500 cc	40.0
2421	pH readjusted to 5, above procedure repeated, 10 min, Eh= 1100mv	87.7
2424	pH readjusted to 5, above procedure repeated, 5 min, Eh= 1100mv	88.7

Notes:
- Starting solution composition (gpl): 2.93 Ni, 2.47 Cr, 0.06 Fe, 0.11 Zn, 0.09 Cu, 0.28 Cd, 0.04 Al
- 500 cc solution from sequential test series four. Solution treated previously for iron, copper and zinc removal. Solution doped with Cr to achieve reported concentration.
- pH adjusted to 5 then chlorine added at 0.2 l/min until pH was lowered and the solids all redissolved. Procedure repeated three times.

The results presented in Table 8.97 show that reasonably effective chromium oxidation occurs at a pH of 5 if the Eh of the solution is maintained > 1000 mv. Poor chromium oxidation is achieved at lower pH values. The results presented in Table 8.98 show that the rate of chromium oxidation may be greater if a cyclic precipitation-oxidation sequence is followed.

Large scale testwork resulted in effective slurry oxidation of chromium, i.e., >80% conversion. All unoxidized Cr^{+++} remains as chromium hydroxide and can be conveniently recycled to the original leach unit operation. The results of the large scale testwork are presented in Table 8.99. The 30-liter test resulted in producing a solution (1.65 gpl Cr) that was almost completely oxidized (95%). The 75-liter test resulted in producing a solution (83.6% of the chromium oxidized) that contained 2.28 gpl Cr (95.2% Cr^{+6}, 4.8% Cr^{+3}).

Most of the unoxidized chromium remaining in the system after oxidation was present as solid $Cr(OH)_3$. This solid can be recycled to the leach system and, therefore, does not represent a loss of chromium.

The large scale testwork showed a greater time required for effective oxidation than the small scale tests. The main reason for this is that the sparging system in the large scale testwork did not produce as efficient gas-solution-solid contact interfaces. It was thought that this difficulty could be overcome by modifying the sparging reactor design. This did not, however, prove to be true.

8.9.1.1.2. Phase II Study

Additional large scale testwork was performed on chlorine oxidation of chromium during the Phase II study. The use of a chlorinator was investigated. Such devices find widespread use in many industries.

A chlorinator in its simplest design resembles an aspirator commonly used in laboratories; a schematic drawing is presented in Figure 8.21. Liquid is pumped through a venturi orifice. The solution flow creates a low pressure at a side port. Chlorine is sucked into the aspirating chamber through the side

TABLE 8.99. CHROMIUM OXIDATION IN LARGE SCALE SEQUENTIAL TESTWORK

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
	30 Liter Test							
2181a	Starting Solution before pH adjust (pH = 1.3, Eh = 380 mv)	0.08	0.01	0.13	1.69	2.54	0.24	0.41
2361	Starting solution adjusted to pH = 5.0	< D.L.	0.001	< D.L.	0.27	1.75	0.23	< D.L.
2340	One hr sample, exposed periodically to Cl_2; Eh maintained at 1000 mv and pH 4.	0.04	0.01	0.08	1.15 (42% oxidized)	2.14	0.25	0.02
2347	A portion of above solution (3.5 lit.) re-exposed to flowing Cl_2, 1.5 hr	0.07	< 0.01	0.11	1.65 (>95% oxidized)	2.31	0.24	0.10
	75 Liter Test							
2564	Starting Solution before pH adjust	0.04	0.22	0.07	2.67	1.75	0.11	0.39
2574	Two hr exposure	0.03	0.08	0.05	1.70 (52.[illegible] oxid.)	1.45	0.09	0.19
2589	Five hr exposure	0.03	D.L.	0.06	2.28 (83.6% oxid.)	1.68	0.11	0.08

Note: . Detailed experimental results presented in Table 8.126, 8.127.

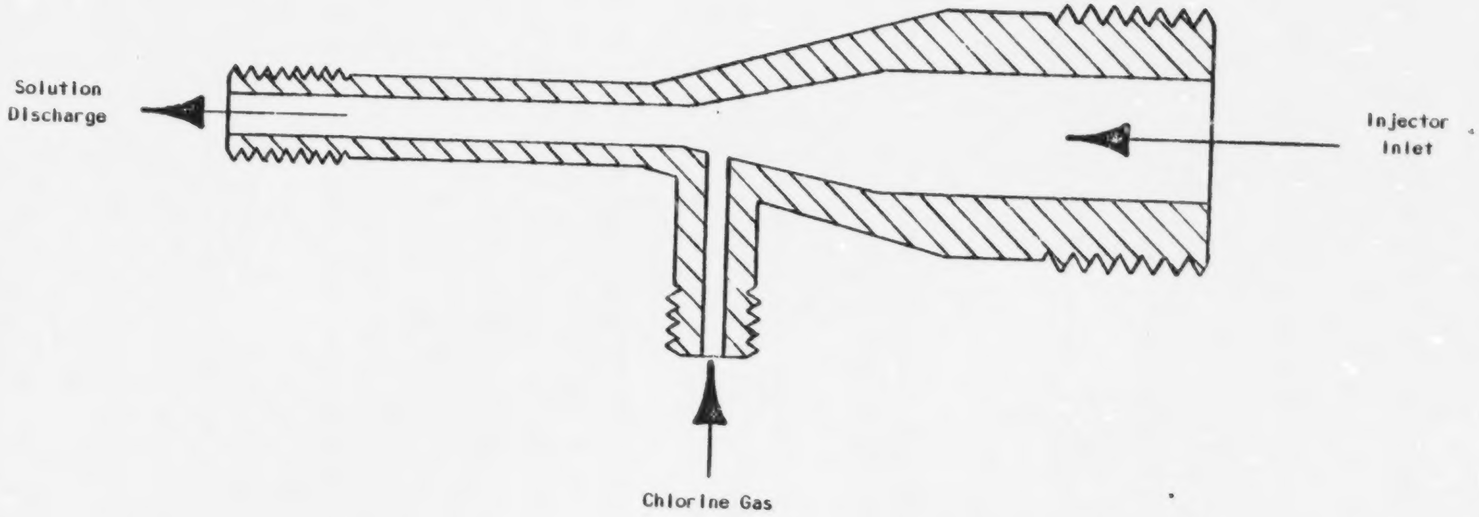

Solution
Discharge
Injector
Inlet
Chlorine Gas

Figure 8.21. Schematic drawing of chlorinator.

port. Turbulence is created in the liquid and good gas (chlorine)-liquid contact is achieved.

Chromium is more effectively oxidized in a slurry where the chromium is present as chromium hydroxide (pH = 4-5):

$$Cr_2(SO_4)_3 + 6\ NaOH \longrightarrow 2\ Cr(OH)_{3(solid)} + 3\ Na_2SO_4$$

$$2\ Cr(OH)_3 \longrightarrow 2\ HCrO_2 + 2\ H_2O$$

$$2\ HCrO_2 + 4\ H_2O + 3\ Cl_2 \longrightarrow 2\ H_2CrO_4 + 6\ HCl$$

Hydrochloric acid is generated and must be neutralized with caustic so that the solution alkalinity remains at a pH of 4-5.

Some nickelous hydroxide may be formed as a solid under the chlorinating conditions but the quantity is small and the residual chromium hydroxide and the nickelous hydroxide can be recycled to the original leach unit operation.

A photograph of the oxidation system is presented in Section 8.14. A schematic representation of the system is presented in Figure 8.22. The system consisted of two 100 liter tanks. Tank A and B were connected so that solution slurry could flow easily from tank B to tank A. Tank A was the feed tank; the slurry solution in each tank was agitated. The slurry in Tank A was pumped to the chlorinator. Discharge from the chlorinator flowed into tank B. Solution pH was maintained in tank B by a pH controller. Shut-off valves placed on the inlet and discharge lines prevented loss of liquid from the piping.

Each oxidation test was begun by placing 120 liters of chromium and nickel containing leach solution in tanks A and B. Agitators were turned on. The pH controller was set with a low limit pH value so that when the pH value was reached or sensed, the controller would activate the small feed pump to add caustic to the tank.

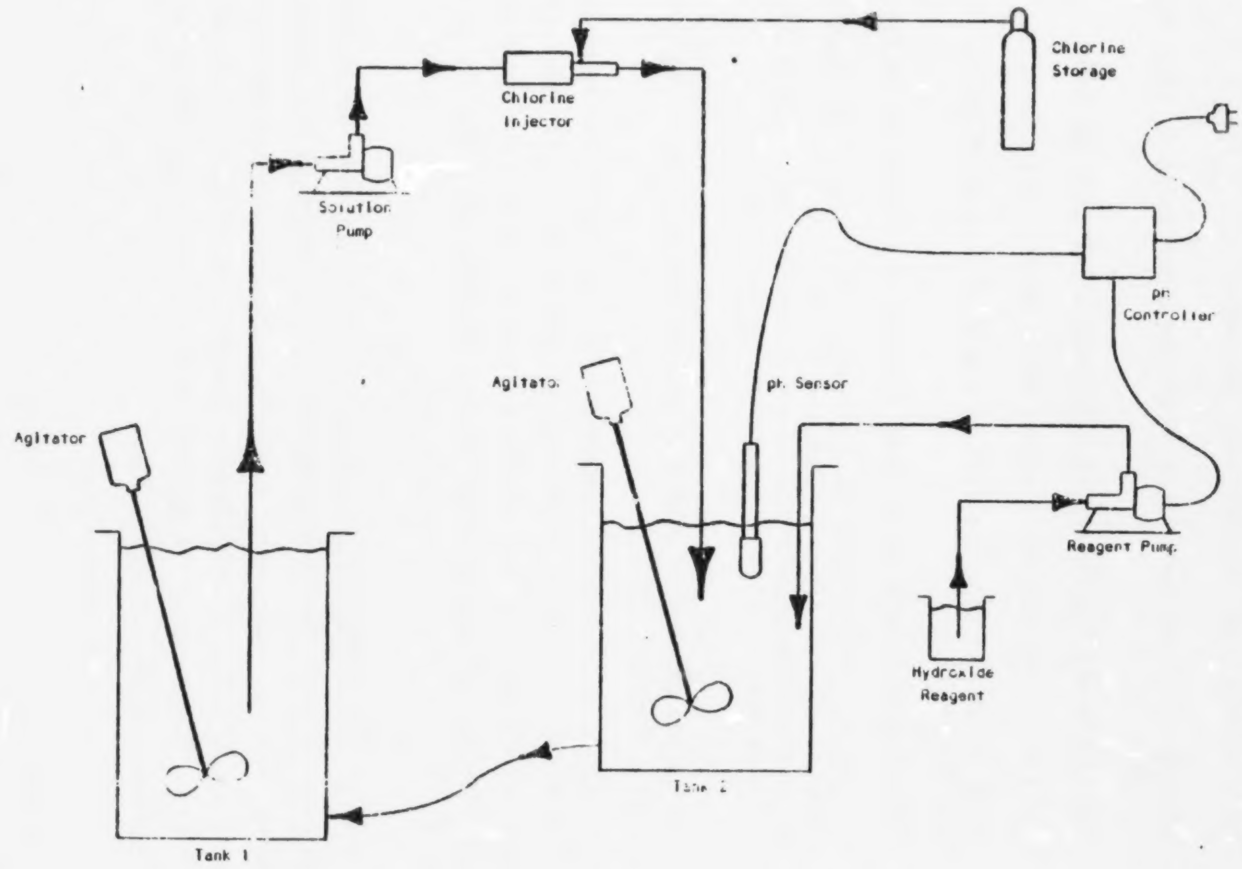

Chlorine Storage
Chlorine Injector
Solution Pump
pH Controller
pH Sensor
Agitator
Agitator
Reagent Pump
Hydroxide Reagent
Tank 1
Tank 2

Figure 8.22. Schematic drawing of the chlorinator system.

Several shakedown tests were performed to observe operations and to identify potential problems. Flow problems, plug-ups, and contact problems were noted and corrected.

The following sampling technique was used:

- Samples of slurry were taken from tank B periodically as a function of time.
- The sample was vigorously agitated and an aliquot was taken.
- The aliquot was acidified with a known amount of sulfuric acid.
- Total Cr and Ni were analyzed in the acidified solution (solids had redissolved).
- The original sample was allowed to stand and solids to settle.
- All aliquot of the solution was taken. This sample represents the filtrate of the chlorine oxidation operation in an actual solid-liquid separation that would be carried out commercially. Chromium and nickel were determined in the liquor.
- A second solution aliquot was taken from the settled sample. The liquid was exposed to Rohm and Haas ion exchange resin IR-900 (an anionic exchange resin).

Chromium anions are extracted (exchanged for $SO_4^=$ ions); chromium cations (Cr^{+++}) are not extracted. Therefore, by measuring the effluent solution for chromium the concentration of oxidized chromium can be determined by difference between the total chromium going into the exchange resin and the chromium carryout.

The results of the large scale chlorination testwork are presented in Tables 8.100-8.102. The results show only up to about seventy percent chromium oxidation in a nine hour period exposure. The previous testwork using a sparging system resulted in oxidation conversions of over eighty percent in four hours. At this point it appears that electrochemical oxidation is the more appropriate approach to follow.

TABLE 8.100. CHLORINE OXIDATION OF CHROMIUM: LARGE SCALE TEST

Exposure Time	Slurry (gpl)		Decant (gpl)		Oxidation (%)
	Cr^{Total}	Ni^{Total}	Cr^{Total}	Cr^{+3}	
Starting	2.02	3.38	1.06	0.38	33.7
1 Hr	2.02	3.16	1.25	0.42	41.1
2	2.02	3.02	1.48	0.30	58.4
3	2.02	3.24	1.45	0.23	60.4
4	2.34	2.98	1.45	0.11	57.3

Notes; .pH maintained at ~ 4.5.
.Starting slurry was from a previous shakedown test.
.Chlorine feed rate 0.17 lb/hr.

TABLE 8.101. CHLORINE OXIDATION OF CHROMIUM: TEST TWO

Exposure Time	Slurry (gpl)		Decant (gpl)		Oxidation (%)
	Cr^{Total}	Ni^{Total}	Cr^{Total}	Cr^{+3}	
1 Hr	2.72	5.84	1.29	0.75	19.8
2	2.52	5.32	1.05	0.57	19.0
3	2.52	5.70	1.12	0.44	27.0
4	2.72	5.70	1.40	0.29	40.8
5	2.58	5.08	1.54	0.17	53.1
6	2.86	5.46	1.68	0.05	57.0
7	2.66	4.83	1.81	0.03	67.0
8	2.80	4.83	1.89	0.04	66.1
9	2.66	4.83	1.81	0.03	67.0
Re-exposed above solution, pH raised from 4.5 to 5.5.					TEST THREE
1	3.94	4.83	3.09	0.03	77.7
2	4.15	4.37	3.06	0.03	73.0
3	4.21	4.70	2.97	0.03	69.8
4	4.27	5.06	2.92	0.03	67.7
5	3.94	4.70	2.92	0.03	73.3
10	4.17	5.06	2.86	0.02	68.0

Notes; . Chlorine feed rate 0.42 lb/hr.
. See text for details

TABLE 8.102. CHLORINE OXIDATION OF CHROMIUM: TEST FOUR.

Exposure Time	Slurry (gpl)		Decant (gpl)		Oxidation (%)
	Cr^{Total}	Ni^{Total}	Cr^{Total}	Cr^{+3}	
Starting Solution	4.24	5.15	0	0	-
1 Hr	4.52	5.05	0.76	0.02	16.4
2	4.57	5.05	1.24	0.03	26.5
3	4.46	4.93	1.47	0.03	32.3
4	4.46	4.71	2.09	0.05	45.7
5	4.52	4.71	2.45	0.05	53.1

Notes:
- pH maintained at ~ 5.5
- Chlorine feed rate at maximum rate for system, 0.42 lb/hr.

8.9.1.2. Electrochemical Oxidation

8.9.1.2.1. Phase I Study

Chromium can be electrochemically oxidized in a compartmentized electrolytic cell. The technology has been developed by the U.S.B.M.(41) at Rolla, MO, and is commercially available, e.g., Scientific Control Laboratories. A schematic diagram is presented in Figure 8.23. The system consists of a series of cells made up of an anode chamber where Cr^{+3} is oxidized to $Cr_2O_7^{-2}$ and a cathode chamber where metal ions are deposited. The chambers are separated by ion selective membranes such as DuPont Nafion 423. These membranes are cation selective, i.e., they allow only cations to pass into the cathode chamber. The separation membrane is necessary in order to prevent oxidized chromium from being reduced at the cathode.

Pilot studies by U.S.B.M. have shown successful oxidation of Cr^{+3} at energy consumptions of 9 kw hour per kg $Na_2Cr_2O_7$ produced.

Preliminary experiments have been performed in the Montana Tech laboratory to study the potential for application of this oxidation technique to the present type of solutions. A schematic diagram of the test cell is presented in Figure 5.10. The preliminary experimental results are presented in Table 8.103.

8.9.1.2.2. Phase II Study

Electrochemical oxidation of chromium was further investigated on a larger scale in the Phase II study. The experimental system was described previously in Section 5.3.2 and 6.3.6. Schematic drawings of the system were presented in Figure 5.11 and 5.12. Photographs of the system are included in Section 8.14.

The electrochemical cell consisted of two box chambers capable of treating about 14 liters of anolyte and 26 liters of catholyte in a batch or continuous mode of operation.

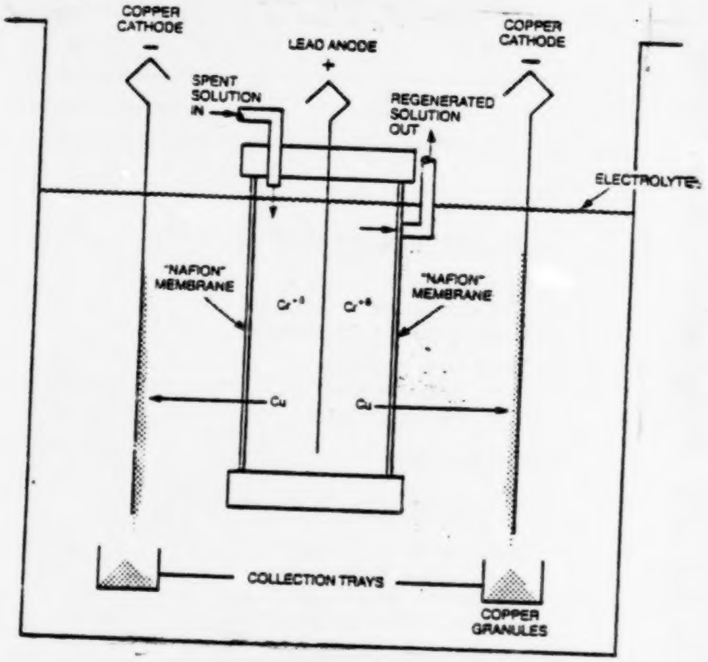

COPPER CATHODE
−
LEAD ANODE
+
COPPER CATHODE
−
SPENT SOLUTION IN
REGENERATED SOLUTION OUT
ELECTROLYTE
"NAFION" MEMBRANE
Cr^{+3}
Cr^{+6}
"NAFION" MEMBRANE
Cu
Cu
COLLECTION TRAYS
COPPER GRANULES

Figure 8.23. Electrochemical cell for oxidation of chromium. (Supplied by Scientific Control Laboratories, Inc.)

TABLE 8.103. ELECTROCHEMICAL OXIDATION OF CHROMIUM: PRELIMINARY TESTWORK

Sample No.	Condition	Chromium Oxidation Extent (%)
	Batch Test	
2664	Starting Solution (2.90 gpl Cr^{+3})	
	Exposure of 1.1 liters of solution to 3 volts at 8 amps, C.D. = 20 amps/ft^2.	
2665	Three hour exposure	69.9
2667	Four hour exposure	84.3
2670	Five hour exposure	89.3
	Continuous Test	
2664	Starting Solution (2.90 gpl Cr^{+3})	
	Exposure of 1.1 liters of solution flowing at 3-5 cc/min to 3.5 volts at 12 amps, C.D.= 20 amps/ft^2.	
2678	One and one half hour exposure	69.5
2683	Three hour exposure	75.4
2689	Six hour exposure	81.6

Notes:
- Cell description presented in Figure 5.8.
- Starting solution was zinc raffinate from the large scale test solution, sequential test series five. Iron, Cu, and were removed prior to use in this study.
- Batch Test Conditions: The cell was loaded with: anolyte - 1.1 liters of leach solution. catholyte - 2.3 liters of 180 gpl H_2SO_4.

The solution was exposed for a period of time, then sampled. The solution was subjected to an anion exchange resin (IRA - 900) to remove all Cr_2O_7 from solution. The effluent solution free of $Cr_2O_7^=$ was analyzed for chromium; the resin was washed to remove entrapped solution and this solution was analyzed for chromium. The oxidized chromium was then calculated from the mass distribution data.

- Continuous Test: The cell was loaded with

anolyte - 1.1 liters of composited batch test solution.
catholyte - 2.3 liters of 180 gpl H_2SO_4.

The solution was fed for 1.5 hours at 5 cc/min then for 3 hours at 3 - 4 cc/min. Solution was sampled as a function of time and analyzed as described above. The chromium in the composited final solution was 75.3 % oxidized; the pH was 0.33, Eh was 866 mv.

Initial tests were conducted using an anode:diaphragm:cathode surface area ratio of 1:1:1. Applied voltage was 3.5v-4.5v, current density was 8-20 amp/ft^2. Static batch test results are reported in Table 8.104. Approximately 85% oxidation was achieved within 21 hours. Further exposure had no apparent effect.

Three continuous tests were performed. The solution flowrates were 10 cc/min. for additive leach solution and discharge anolyte. The catholyte was withdrawn and recirculated back into the catholyte chamber. A perforated lead wool anode was used to ensure a high contact surface area. Lead sheet cathodes were used. The anode surface area available to the solution is unknown, the physical outer holding plate area was 1.8 ft^2. The cathode surface area was 1.32 ft^2.

The results of the first continuous test series are presented in Table 8.105. The anolyte chamber was filled with fully oxidized chromium; unoxidized leach solution was fed into the chamber at a rate of 10 cc/min. The effluent stream showed 81% of the chromium oxidized.

A second test series was run for 48 hours using the anolyte from Series One, Table 8.106. The conversion achieved in this test was 87.2%. A third series of tests were conducted using a new catholyte, Table 8.107. Steady state conditions appear to be established after about 48 hours at a conversion rate of about 90% of the chromium.

The Nafion membrane allows cations to pass through but not anions. If the assumption is made that no solution leaked from the anode chamber to the cathode chamber then migration of nickel can be determined. A determined effort was made to prevent leakage, therefore, the assumption is probably reasonable. If Cr^{+6} had been analyzed in the catholyte then leakage could have been detected. This analysis was, however, not performed. The nickel migration results are presented in Table 8.107.

8.9.1.3. Oxidizing Properties of SO_2-O_2 System

An alternate (perhaps low cost) means of oxidizing chromium may be by a relatively new technology developed by INCO$^{(42)}$, i.e., an SO_2-O_2 system. INCO

TABLE 8.104. BATCH ELECTROCHEMICAL OXIDATION OF CHROMIUM

Sample No.	Condition	Chromium Concentration (gpl)			
		Anolyte		Catholyte	Chromium Oxidized (%)
		Cr^{+6}	Cr^{+3}	Cr^{Total}	
5000B	Starting Solu.	0.14	2.91	0.16	-
5001	21 Hrs	2.72	0.27	0.22	84.9
5002	24	2.73	0.23	0.20	86.4
5003	48	2.54	0.23	0.42	85.4

Notes:
- Starting anolyte (pH = 1.0) and catholyte from a previous test. Catholyte 180 gpl H_2SO_4.
- Perforated anode, 4.5 volts, 14.5 - 19.0 amps/ft^2
- Solution air agitated.

TABLE 8.105. CONTINUOUS ELECTROCHEMICAL OXIDATION OF CHROMIUM: SERIES ONE

Sample No.	Condition	Chromium Concentration, gpl			Chromium Oxidation, %
		A		C	
		Cr^{+6}	Cr^{+3}	Cr^{total}	
5004	Starting Anolyte	2.77	--	--	
5005	Feed Anolyte, 68 lit.	--	1.54	--	
5006,7	120 Hours	1.42	0.34	0.61	78.0

NOTES:
- A = anolyte, C = catholyte
- Anolyte feed pH = 1.0 and withdrawn continuously at 10 cc/min., catholyte recirculated at 10 cc/min., air agitation used.
- Perforated lead anode, 4.5 v, 16.7 - 18 amp/ft^2.
- Catholyte contained 180 gpl H_2SO_4.

TABLE 8.106. CONTINUOUS ELECTROCHEMICAL OXIDATION OF CHROMIUM: SERIES TWO

Sample No.	Condition	Chromium Concentration, gpl			Chromium Oxidation, %
		A		C	
		Cr^{+6}	Cr^{+3}	Cr^{total}	
5009	Starting Anolyte	1.42	0.34	--	
5010	Feed Anolyte	--	1.79	--	
5011,12	24 Hrs.	1.22	0.35	0.23	80.4
5013,14	48 Hrs.	1.70	0.23	0.24	87.2

NOTES: ·Conditions same as presented in Table 8.105.

TABLE 8.107. CONTINUOUS ELECTROCHEMICAL OXIDATION OF CHROMIUM: SERIES THREE

Sample No.	Condition	Chromium Concentration, gpl			Chromium Oxidation, %
		A		C	
		Cr^{+6}	Cr^{+3}	Cr^{total}	
5024	Starting Anolyte	13.95	0.15	0.01	
5025	" Catholyte			0.01	
5023	Feed Anolyte	--	2.40		
5026,7	24 Hrs.	11.36	0.44	0.12	81.7
	Diaphragm Washed				
5028	New Feed Anolyte		2.73		
5029	New Anolyte	25.3			
5030	Catholyte Unchanged			0.12	
5031,32	24 Hrs.	19.8	0.45	0.30	83.5
5033,34	48 Hrs.	13.9	0.30	0.35	89.0
5037,38	96 Hrs.	9.76	0.35	0.61	87.1
5039,40	120 Hrs.	8.04	0.12	0.71	95.6

NOTES:
- A = anolyte, C = catholyte
- Anolyte feed (pH = 1.0) continuously at 10 cc/min., catholyte recirculated but not withdrawn.
- Perforated lead anode, 4.5 v, 22.5 amp/ft^2.

TABLE 8.108. NICKEL MIGRATION THROUGH NAFION DIAPHRAGM DURING SERIES THREE CHROMIUM OXIDATION TESTWORK

Sample No.	Condition	Nickel Migration, %	
		During Period	Cumulative
5031,32	24 Hr. Exposure	15.9	15.9
5033,34	48 " "	8.6	24.5
5035,36	72 " "	11.1	35.6
5037,38	96 " "	6.6	42.2
5039,49	120 " "	6.3	48.5

NOTES:
- Conditions given in Table
- Starting nickel concentration in anolyte: 0.86 gpl
- Feed nickel concentration in anolyte: 2.86 gpl
- Starting nickel concentration in catholyte: 0.03 gpl.

studies have shown that use of SO_2-O_2 mixtures produce a powerful oxidizing specie in the presence of a variety of metal ions. They postulate that under favorable pH conditions the oxidant is formed by reaction of oxygen with metal sulfite complexes, i.e., activated complexes like $<MeSO_5>^{-2}$ form and serve as the oxidizing specie. The pH level required depends on what metal ion is to be oxidized. Chromium oxidation has not been investigated. However, if the system were applicable to chromium a rather low cost oxidizing system may be possible; i.e., perhaps a considerably lower cost than the chlorine oxidizing system or electrochemical oxidation system.

The SO_2-O_2 approach is seen to have potential possible future application for oxidation of chromium but the technology is not at present demonstrated for chromium oxidation and is, therefore, not considered as a viable alternate for the present study. The system is, however, included in the cost analysis, Section 8.15.

8.9.2. Sludge Oxidation by Roasting

Oxidation by roasting may be the only feasible approach for high iron-high chromium sludge materials because of the chromium loss during iron removal by jarosite precipitation. The concept of oxidation roasting is that Cr^{+3} is converted to Cr^{+6} (as CrO_4^{-2}) which reacts in the presence of sodium to form sodium chromate. Sodium chromate is soluble at all pH values, therefore, it can be dissolved by a water leach in preference to all other metals.

Only a few preliminary tests have been conducted during the present study. The results are encouraging and indicates a possible research direction for high chromium sludge material. The preliminary test results are summarized in Tables 8.109. and 8.110.

8.10. CHROMIUM EXTRACTION

Chromium is present in mixed metal sludge leach solutions in relatively low concentrations: usually <2-4 gpl. Therefore, a means of concentration (in addition to selective removal) is required.

TABLE 8.109. ROAST-LEACH TEST ON HIGH CHROMIUM SLUDGE: PRELIMINARY TESTS

Sample #	Condition	Cr Extraction (%)
	200°C Roast	
1237	1 hr.	18.9
1238	4 hr.	10.8
1239	4 hr., NaOH	32.6
	400°C Roast	
1240	1 hr.	4.6
1241	4 hr.	10.2
1242	4 hr., NaOH	90.6
	600°C Roast	
1243	1 hr.	4.3
1244	4 hr.	1.4
1245	4 hr., NaOH	97.3
1246	Untreated Sludge	63.6

NOTE: ·Starting Solid Composition (%): 15.64±.0.46 Cr, 0.71±0.05 Fe; 0.71±0.02 Cu, 1.16±0.04 Ni, 0.06±.02 Zn, Cd < D.L., 5.44±0.07 Al

·10 gm dry sludge roasted in air

·NaOH added to some tests at a dose of 1 gm NaOH/gm sludge

·Non-NaOH containing solids leached (10% solids) under standard H_2SO_4 leach conditions for 0.5 hrs

·NaOH containing solids leached at pH = 10-11, 10% solids

TABLE 8.110. ROAST LEACH ON HIGH CHROMIUM SLUDGE: TESTWORK

Sample #	Condition	Cr Extraction (%)
	400°C Roast, 2 Hours	
1262	5 gm sludge, 5 gm NaOH, 2.5 gm Na_2O_2	39.2
1263	5 gm sludge, 5 gm NaOH	70.0
1264	10 gm sludge, 10 gm NaOH	72.9
	600°C Roast, 2 Hours	
1265	5 gm sludge, 5 gm NaOH 2.5 gm Na_2O_2	71.4
1266	5 gm sludge, 5 gm NaOH	84.2
1267	10 gm sludge, 5 gm NaOH	87.2
	800°C Roast, 2 Hours	
1269	5 gm sludge, 5 gm NaOH	50.4
1270	10 gm sludge, 10 gm NaOH	62.4
1355	Untreated solid sludge leach	0.6

NOTE: ·Starting Solid Composition (%): 17.86±.20 Cr, 0.36±0.07 Fe, 0.94±0.10 Cu, 0.69±0.13 Ni, 0.06±0.03 Zn, < D.L. Cd, 0.35±0.03 Al

·All roasts conducted in open crucibles in a box furnace. NaOH added as a solution (500 gpl) to dry sludge powder.

·All roasted solids were leached: 10 w/o solids, 0.5 hr., 25°C, pH = 7.

If the chromium has not been oxidized then a conceptual modification of the flowsheet presented in Figure 6.1 is that after Fe, Cu, Zn removal, nickel can be removed by sulfide precipitation. A design matrix illustrating such a separation is presented in Table 8.111. Further testwork has not been conducted but the approach shows a possible alternative treatment procedure. It would mean that the resulting solution would have to be further treated to recover the Cr^{+3}.

After chromium oxidation, as described in sections 6.3.6 and 8.9.1.1. the solution contains only Cr^{+6} (as $Cr_2O_7^{=}$) and Ni^{+2} with only small residual concentrations of other metal ions. Chromium (+6) can be separated from the leach solution by: 1) precipitation, 2) ion exchange using an anion exchange resin or 3) by solvent extraction.

8.10.1. Lead Chromate Precipitation

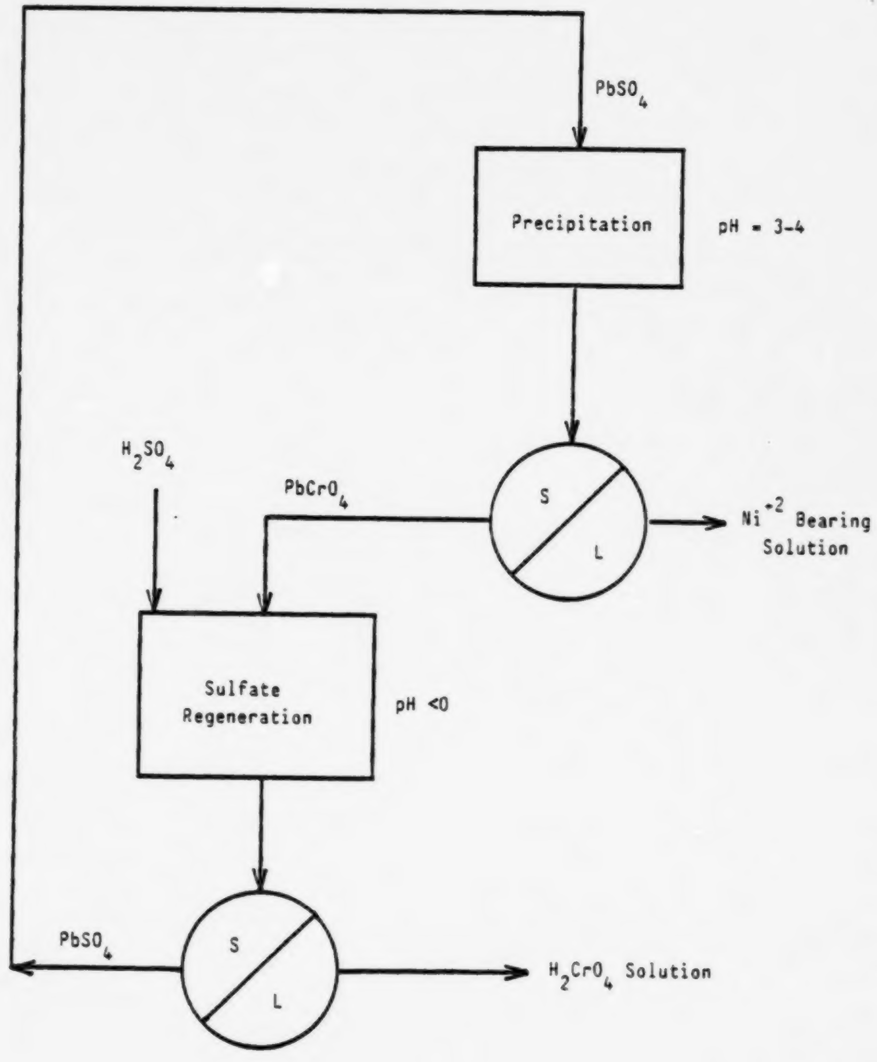
Chromium can be selectively precipitated from a sulfate solution by lead cations, i.e., the Cr^{+6} concentration in equilibrium with lead chromate at a pH = 3.1 is 0.87 mg/l. Therefore, lead cations should strip Cr^{+6} from an acid solution at a pH value near the solution pH resulting from the previous oxidation unit operation. The chromium stripping process is illustrated in Figure 8.24.

Small scale testwork was conducted to determine the extent of amount of $PbSO_4$ added. The results are presented in Table 8.112 and show that effective chromium removal is achieved at pH values in the range 4-5.

The results of large scale lead chromate precipitation are presented in Table 8.113. The data show that chromium can be effectively stripped from solution, i.e., chromium levels of 8 mg/liter were achieved.

8.10.2. Chromium Solvent Extraction

Solvent extraction literature(5) shows that Cr^{+6} as the anions, chromate or dichromate, can be selectively extracted from acidic sulfate solutions by Alamine 336 (a Tertiary Amine) and Aliquot 336. The extraction is pH



$PbSO_4$
Precipitation
pH = 3-4
H_2SO_4
$PbCrO_4$
S
L
Ni^{+2} Bearing Solution
Sulfate Regeneration
pH <0
$PbSO_4$
S
L
H_2CrO_4 Solution

Figure 8.24. Chromium Removal by Lead Precipitation

TABLE 8.111. DESIGN MATRIX FOR SELECTIVELY REMOVING NICKEL FROM CHROMIUM (CR^{+++}) SOLUTION (FULL REPLICA)

Results: Extraction from Solution (%)

Sample		Solution pH	Time (min.)	Amount Na_2S (Stoich.)	Ni	Cr
	Base	2.5	15	1.5		
	Unit	1	5	.5		
	High (+)	3.5	20	2.5		
	Low (-)	1.5	10	1.0		
	Test #				Ni	Cr
2020	1	-	-	-	22.6	5.6
2030	2	+	-	-	89.2(90.4)	12.1(13.2)
2021	3	-	+	-	24.9	7.0
2031	4	+	+	-	88.7	8.2
2022,	5	-	-	+	44.9(24.0)	5.3(3.3)
2032	6	+	-	+	99.0	11.8
2024	7	-	+	+	22.1	5.6
2033	8	+	+	+	99.5	9.8
2026	Base				83.1±1.5	8.1±0.4
Effects (%)						
Ni		32.7	-2.6	5.0		
Cr		2.3	-0.5	0		

NOTE:
- ·Synthetic Solution: 4 gpl Ni^{++}
  2 gpl Cr^{+++}
- ·Na_2S solution added, usually slowly but complete with 10-15 min.
- ·Product filtered easily

TABLE 8.112. CHROMIUM REMOVAL BY LEAD CHROMATE PRECIPITATION

Sample No.	Conditions	Chromium Precipitated (%)
2197	Starting Solution (0.31 gpl Cr) Oxidized with Cl_2 for one hour at pH = 1.5.	
2289	Contacted with 5 g $PbSO_4$	0
2291	Contacted with 10 g $PbSO_4$	0
2215	Starting Solution (0.31 gpl Cr) Oxidized with Cl_2 for one hour at pH = 3.7.	
2297	Contacted with 5 g $PbSO_4$	65.5 (pH decreased to 3.4)
2299	Contacted with 10 g "	62.9 (")
2226	Starting Solution (0.31 gpl Cr) Oxidized with Cl_2 for one hour at pH = 3.9.	
2301	Contacted with 5 g $PbSO_4$	86.6
2303	Contacted with 10 g "	89.8
2206	Starting Solution (2.61 gpl Cr) Oxidized with Cl_2 for one hour at pH = 1.3.	
	Contacted with 5 g $PbSO_4$	0
	Contacted with 10 g "	0
2237	Starting Solution (2.61 gpl Cr) Oxidized with Cl_2 for one hour at pH = 4.0	
2305	Contacted with 5 g $PbSO_4$	95.6 (pH decreased to 2.8)
2307	Contacted with 10 g "	95.2 (")
2311	Solution 2307 readjusted to pH = 5. Contacted with 5 additional grams of $PbSO_4$.	88.3 additional removal

Notes: 100 cc exposed to chlorine; pH maintained during oxidation; pH adjusted to desired level; contacted with $PbSO_4$ for 10 minutes.

TABLE 8.113. LARGE SCALE TESTWORK ON LEAD CHROMATE PRECIPITATION

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
	42 Liter Test							
2600	Starting Solution, pH = 4.2.	0.03	0.03	0.06	2.34	1.57	0.10	0.16
2601	Five min. exposure to 1X stoichiometric requirement of $PbSO_4$, pH = 4.7	0.03	< D.L.	0.06	0.80	1.60	0.10	0.09
2602	Thirty min. exposure to 2X stoichiometric requirement of $PbSO_4$, pH = 3.8	0.03	< D.L.	0.07	0.007	1.62	0.10	0.14

Note: . Detailed experimental results presented in TABLE 8.127.

independent and can be applied over the range pH 1-7. The disadvantage is that the amine reagents are degraded by acidic solutions over long periods of time(5).

8.10.3. Dichromate Ion Exchange

Anionic ion exchange (IX) is a means of selectively extracting chromium anions from chromium-nickel sulfate solutions, e.g., Rohm and Haas IRA 900 (a strongly basic IX resin) will quantitatively remove chromium anions from Cr-Ni solutions. However, recovery of the chromium from the resin by stripping with NaOH is difficult. Stripping can be accomplished but large volumes of strip solution are required. Therefore, the concentration of the recovered chromium is rather low. This is a distinct disadvantage because weak chromium bearing solutions require concentration by solution evaporation which adds cost to the overall recovery process.

An additional potential problem with IX resins is degradation by the leach solution, especially highly oxidizing solutions such as high concentration dichromate bearing solutions. Repeated load/strip testwork in the present study definitely released the characteristic ammonia odor to the laboratory.

Chromate recovery from plating rinse waters is commercially practiced on solutions of low chromium content (<100 mg/l) and at pH values in the range of 4.5-5.0 using a weakly basic anion exchange resin, e.g., IRA 94. Such solutions are drastically different from those solutions considered in this study, e.g., the present leach solutions are highly oxidizing and contain much higher chromium concentrations.

8.11. NICKEL EXTRACTION

The nickel concentration in the treated large scale leach solution is in the range of a few grams per liter. Leach tests on segregated sludge materials produced nickel contents up to 42 gpl. However, most mixed metal sludges produced nickel contents in the range 2-6 gpl. A means of recovering the nickel from solution and/or concentrating it in solution is required.

8.11.1. Sulfide Precipitation

Nickel sulfide can be effectively precipitated from a nickel bearing solution by the addition of a sodium sulfide solution. If the sulfide solution is added at the proper concentration and rate there is no release of hydrogen sulfide gas. The pH of the leach solution following lead chromate precipitation is 4-4.5. It is desirable to maintain the pH at this level (or even higher is better) to prevent the release of hydrogen sulfide gas.

The results of sulfide precipitation from the large scale tests are presented in Table 8.114. The nickel content was decreased to six mg/liter, the chromium content to four mg/liter, and all other metal values to below their detection limit.

Realistically the amount of sulfide added to precipitate the nickel would be chosen to less than the nickel stoichiometric requirement. It would not be a problem if some of the nickel were left in solution since most (>90%) of the final solution is needed as make-up water in the leach unit operation. A deficiency of sulfide would be required because if sulfide existed in the make-up water then H_2S would be produced in the leach stage.

An alternative treatment approach would be to precipitate nickel hydroxide along with the lead chromate by raising the pH to the range 6-9. The residue could then be releached in ammonium carbonate to redissolve the nickel hydroxide as a nickel amine. The lead chromate would not be dissolved.

The advantages of this approach are two-fold. First, the filtrate from the lead chromate-nickel hydroxide precipitate solid/liquid separation could be recycled without fear of H_2S generation in the leach stage and the ammonium leaching of the residue would produce a concentrated nickel solution that could be treated to produce nickel sulfate, nickel carbonate, or other nickel compounds.

8.11.2. Solvent Extraction

Commercial solvent extraction of nickel from sulfate solutions is not extensively practiced. The equilibrium distribution diagrams show that nickel

TABLE 8.114. LARGE SCALE TESTWORK ON NICKEL SULFIDE PRECIPITATION

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
2605	Starting Solution, sequentially treated test series five, pH = 4	0.04	< D.L.	0.06	0.01	1.67	0.10	0.10
2606	Ten min. exposure	< D.L.	"	"	"	1.53	< D.L.	"
2607	Twenty min. exposure	"	"	< D.L.	0.007	0.02	"	"
2609	Forty-five min. exposure	"	"	"	0.005	0.005	"	"
2610	Sixty min. exposure	"	"	"	0.004	0.006	"	"

Notes:
- Detailed experimental results presented in Table 8.127.
- Sodium sulfide (325 gpl) added slowly to solution. Addition (2X stoichiometric requirement) complete after 45 minutes.

is not extracted from sulfate solution at low pH levels, i.e., refer to Figures 8.10a., 8.10b., 8.12., 8.16 for D_2EHPA, VERSATIC Acid 911, LIX-64N. The pH level required for nickel extraction is too high to be applied to a chromium bearing solution, i.e., Cr^{+3} will begin to precipitate at pH levels >2.5-3.5 (depends on concentration in the solution). Therefore, the solvent extraction of nickel as a means of separating Ni^{+2} from Cr^{+3} is not feasible. Solvent extraction of Ni^{+2} from the final leach solution, after Fe, Cu, Zn, and Cr are removed, appears to be possible by D_2EHPA. If the extraction is possible then SX would be a way of concentrating the Ni content into a strip solution and NiS precipitation would be unnecessary. Bench scale shake tests were performed and the results are reported in Tables 8.115.-8.117.

The influence of pH on LIX-64N extraction of Ni was investigated (Table 8.115); about 20 percent extraction was achieved at an initial pH = 4 and pH = 5 in two contacts. At an initial pH of 9 (Table 8.116.) 86 percent was extracted. The use of an NH_4OH, NH_4CO_3 buffer solution gives almost quantitative extraction of Ni (Table 8.117.). However, the problem with the high pH systems is that a portion of the nickel is precipitated from solution as a hydroxide.

Although other investigators have shown extraction of nickel by D_2EHPA at pH values of 5-6, the present test work did not. The results of a series of shake tests are presented in Table 8.118.

Recent developments(43) in SX show that a pronounced synergistic effect occurs when D_2EHPA is mixed with non-chelating aldoximes. The extraction sequence is drastically altered by the presence of the non-chelating aldoxime: order of extraction by D_2EHPA:

Zn>Cu>Fe>Co>Ni

Order of extraction by D_2EHPA plus 2-ethylhexanol oxime (EHO):

Ni>Cu>Co>Fe>Zn

TABLE 8.115. LIX 64N EXTRACTION OF NICKEL AS A FUNCTION OF PH: PH = 4-6.6

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
1370	Potassium Jarosite In-situ precipitation; six-hour exposure	0.42	3.69	2.10	0.54	6.89	0.27	4.65
	Copper Removal Solution 1370 pH adjusted to 1.75. Contacted twice with 20% LIX 622							
1372	First Contact	0.48	0.34	2.10	0.58	7.22	0.30	4.77
1373	Second Contact	0.46	0.010	2.21	0.61	7.65	0.31	5.36
	Zinc Removal Solution 1373 pH adjusted to 2.0. Contacted four times with 40% DEHPA							
1374	First Contact	0.38	0.009	1.73	0.47	2.23	0.24	3.58
1375	Second Contact	0.024	0.010	2.02	0.56	0.83	0.28	3.06
1376	Third Contact	0.013	0.009	1.74	0.47	0.19	0.23	1.53
1377	Fourth Contact	0.007	0.010	2.20	0.60	0.02	0.26	0.64

TABLE 8.115. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
	pH Adjustment (NH_4OH) and LIX 64N (10%) contact.							
1385	Solution 1377 after pH adjusted to 4.0	0.003	0.002	1.22	0.28	0.00	0.14	0.11
1388	Aqueous after first contact (O/A = 1)	<D.L.	<D.L.	1.11	0.25	<D.L.	0.13	0.10
1391	Aqueous after second contact (O/A = 1)	0.002	<D.L.	1.07	0.23	0.008	0.13	0.09
1394	First strip of 1391 (O/A = 1) (150 gpl H_2SO_4)	<D.L.	0.004	0.006	0.001	0.001	0.001	0.001
1397	Second strip of 1391 (O/A = 1) (150 gpl H_2SO_4)	0.001	<0.001	0.015	0.003	0.001	0.002	0.002
	pH = 5.0							
1386	Solution 1377 after pH adjusted to 5.0	<D.L.	<D.L.	1.91	0.089	<D.L.	0.21	<D.L.
1389	Aqueous after first contact (O/A = 1)	0.003	<D.L.	1.82	0.085	<D.L.	0.20	0.003
1392	Aqueous after second contact (O/A = 1)	0.001	<0.001	1.56	0.073	0.004	0.17	<0.001

TABLE 8.115. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
1395	First Strip of 1392	<0.001	<0.001	0.012	<0.001	<0.001	0.001	<0.001
1398	Second strip of 1392	<0.001	<0.001	0.016	<0.001	<0.001	0.001	<0.001
	pH = 6.6							
1387	Solution 1377 after pH adjusted to 6.6	<D.L.	<D.L.	0.91	0.01	0.01	0.07	0.009
1390	Aqueous after first contact (O/A = 1)	0.004	<0.001	1.09	0.01	0.03	0.08	0.009
1393	Aqueous after second contact	0.001	<D.L.	0.98	0.01	0.03	0.08	0.007
1396	First strip of 1393	0.001	<0.001	0.010	0.01	0.001	0.05	0.001
1399	Second strip of 1393	<0.001	<0.000	<0.018	0.00	0.001	<0.01	<0.001

Notes:
. Solution (approximately one liter) treated sequentially to remove Fe, Cu, Zn prior to Ni
. All nickel tests performed in 125 or 250 cc separatory funnels.
. Initial pH readjusted to starting value before each contact.

TABLE 8.116. LIX 64N SOLVENT EXTRACTION OF NICKEL: NH_4OH, NH_4CO_3

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
1377	Starting solution: potassium jarosite solution treated for Cu, Fe, Zn removal	0.007	0.010	2.20	0.60	0.02	0.26	0.64
1433	Solution 1377 (150 cc) buffered with 40 gpl NH_4OH, 40 gpl NH_4CO_3 (250 cc) to pH of 9.0 and filtered	<D.L.	0.003	0.612	0.02	0.00	0.03	<D.L.
1434	Solution 1433 contacted with 10 v/o LIX 64N, 90 v/o 470B; O/A = 1, 3 min., R.T.	<D.L.	<0.001	0.002	0.01	<D.L.	0.03	<D.L.
1435	Repeat of 1434	<D.L.	<0.001	0.002	0.01	<D.L.	0.03	<D.L.
1436	Second contact of aqueous 1434 with 64 N	<D.L.	0.001	<0.001	0.01	<D.L.	0.02	<D.L.
1437	Strip of 1434 organic with 200 gpl H_2SO_4, O/A = 1, 3 minutes	<D.L.	0.003	0.55	0.003	<D.L.	<D.L.	<D.L.
1438	Strip of 1435 organic with 200 gpl H_2SO_4	<D.L.	0.003	0.56	0.004	<D.L.	<D.L.	<D.L.

TABLE 8.116. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
1439	Strip of 1436 organic with 200 gpl H_2SO_4	<D.L.	0.001	0.006	0.002	<D.L.	0.005	<D.L.

NOTE:
. Starting solution treated for Fe, Cu, Zn removal by standard flowsheet practice.
. All tests performed in 125 or 250 cc separatory funnels.
. Temperature: 25-30°C.

TABLE 8.117. BENCH SCALE SEQUENTIAL SOLVENT EXTRACTION TESTWORK

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
1466	Jarosited leach solution; one liter	3.14	1.44	9.37	0.54	4.95	0.52	1.58
1467	Diluted 1466, pH = 1.75	1.56	0.69	4.99	0.27	2.75	0.24	0.63
	Cu SX							
1468	LIX 622 (10v/o) contacted with 1467 (O/A = 1)	0.02	0.69	5.00	0.27	2.74	0.25	0.64
1469	LIX 622 contacted with aqueous from 1468. Initial pH of aqueous to 1.75	0.004	0.68	4.93	0.26	2.71	0.25	0.63
	Zn SX							
1470	Aqueous 1469 adjusted to pH = 2; then contacted (first contact) with DEHPA organic (O/A =1)	0.001	0.63	1.71	0.27	2.76	0.23	0.55
1475	Aqueous 1470 adjusted to pH = 2; then recontacted (second contact) with DEHPA.	< D.L.	0.57	0.32	0.27	2.74	0.19	0.39
1477	Aqueous 1475 adjusted to pH = 2; then recontacted (third contact) with DEHPA.	< D.L.	0.44	0.03	0.25	2.59	0.12	0.16

TABLE 8.117. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
1479	Aqueous 1477 adjusted to pH =2; then recontacted (fourth contact) with DEHPA.	< D.L.	0.35	< D.L.	0.27	2.75	0.05	0.04
	DEHPA Organic Strip (Compositions of aqueous phase presented)							
1471	Organic 1470 stripped with 200 gpl sulfuric acid	< 0.001	< 0.01	3.50	< 0.01	< 0.01	0.02	0.01
1473	Above organic stripped second time with 200 gpl acid	"	"	0.01	< D.L.	< D.L.	< D.L.	< D.L.
1472	Organic 1470 stripped with 150 gpl sulfuric acid	< 0.01	< 0.01	3.36	< 0.01	< 0.01	< 0.02	< 0.01
1474	Above organic stripped second time with 150 gpl acid	< 0.001	< D.L.	0.01	< D.L.	< D.L.	< D.L.	< D.L.
1476	Organic 1475 (second extraction contact) stripped with 200 gpl acid	"	0.01	1.39	0.01	< 0.01	0.04	0.04
1478	Organic 1477 (third extraction contact) stripped with 200 gpl acid	<D.L.	< 0.01	0.26	< 0.01	< 0.01	0.05	0.05
1480	Organic 1479 (fourth extraction contact) stripped with 200 gpl acid	<0.001	< 0.01	0.03	< 0.01	0.02	0.07	0.02
	Ni SX: LIX 64N (10v/o)							
1481	PH raised to 9, filtered	< 0.001	0.13	< 0.001	0.01	1.06	0.02	0.02

TABLE 8.117. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
1482	Aqueous 1481 contacted with LIX 64N (O/A = 1)	< D.L.	0.15	< D.L.	0.13	0.15	0.06	0.02
1484	Organic 1482 stripped with 200 gpl sulfuric acid	< 0.001	0.02	< D.L.	< 0.01	1.30	< D.L.	< 0.01
	Ni SX: LIX 64N (10v/o)							
1485	PH raised to 9 with NH_4OH/NH_4CO_3 mixture (40 gpl each), filtered	< 0.001	0.02	< D.L.	0.02	0.48	< D.L.	< 0.01
1486	Aqueous 1485 contacted with LIX 64N (O/A = 1)	< D.L.	0.02	"	"	0.08	"	"
1487	Organic 1486 stripped with 200 gpl sulfuric acid	< 0.001	< 0.001	"	"	0.35	"	< 0.001

Notes:
- Barrel 14 sludge leached under standard conditions.
- Cu SX: 100cc of aqueous contacted with 100cc of organic, 3 min, ambient temperature, O/A = 1
- Zn SX: 100cc of aqueous contacted with 100cc of organic, 40 v/o DEHPA, conditions as above.
- DEHPA Strip: conditions as for other SX tests.
- Ni SX: conditions as above, pH of aqueous phase raised, solution filtered, then contacted with organic.

TABLE 8.118. DEHPA EXTRACTION OF NICKEL AS A FUNCTION OF SOLUTION PH: PH = 4,5

Sample No.	Condition	Concentration (gpl)						
		Ni	Fe	Cu	Cr	Zn	Cd	Al
1377	Starting solution: potassium jarosite solution treated for Cu, Fe, Zn removal, PH = 1.29	2.20	0.01	0.01	0.60	0.02	0.26	0.64
1458	Solution pH adjusted to to 5.0 and filtered	1.64	----	----	0.21	0.01	0.20	0.01
1459	Solution pH adjusts to 6.0 and filtered	0.88	----	----	<D.L.	<D.L.	0.01	<D.L.
	10 v/o DEHPA - 90 v/o 470B; pH = 5.0							
1442	First contact with 1458 Final pH = 2.6, O/A = 1, R.T., 2 minutes	1.71	0.01	0.01	0.20	0.03	0.11	<D.L.
1443	Strip of 1442 organic with 150 gpl H_2SO_4, O/A = 1	0.03	0.01	0.01	0.01	0.02	0.10	<D.L.
1444	Second contact, aqueous (1442) with 10 v/o DEHPA, O/A = 1, aqueous adjusted to pH = 5.0	1.58	0.01	0.01	0.15	0.01	<D.L.	<D.L.
1445	Strip of 1444 with 150 gpl H_2SO_4, O/A = 1	0.08	0.01	0.01	0.05	0.01	0.12	<D.L.

TABLE 8.118. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Ni	Fe	Cu	Cr	Zn	Cd	Al
	pH = 6.0							
1450	First contact of 10 v/o DEHPA with 1459 aqueous, pH = 6.0	0.87	0.01	<D.L.	0.02	< D.L.	0.03	< D.L.
1451	Strip of 1450 organic with 150 gpl H_2SO_4	0.01	0.01	<D.L.	0.01	< D.L.	0.04	< D.L.
1452	Second contact, aqueous 1459, pH = 6.0	0.77	0.01	<D.L.	0.01	< D.L.	< D.L.	< D.L.
1453	Strip of 1452 organic with 150 gpl H_2SO_4	0.03	0.01	<D.L.	0.01	< D.L.	0.04	< D.L.
	40 v/o DEHPA, 60 v/o 470B							
	pH = 5.0							
1446	First contact, aqueous (1458) with 40 v/o DEHPA, O/A = 1	1.57	0.01	0.01	0.18	0.01	0.02	< D.L.
1447	Strip of 1446 organic with 150 gpl H_2SO_4	0.08	0.01	0.01	0.03	0.01	0.17	< D.L.
1448	Second contact, aqueous (1458) with 40 v/o DEHPA	1.58	0.01	0.01	0.15	< D.L.	< D.L.	< D.L.

TABLE 8.118. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Ni	Fe	Cu	Cr	Zn	Cd	Al
1449	Strip of 1448 organic with 150 gpl H_2SO_4	0.10	< D.L.	0.01	0.04	< D.L.	0.05	< D.L.
1454	First contact, aqueous (1459) with 40 v/o DEHPA	0.80	0.01	< D.L.	0.02	< D.L.	< D.L.	< D.L.
1455	Strip of 1454 organic with 150 gpl H_2SO_4	0.02	0.01	< D.L.	0.01	< D.L.	0.08	< D.L.
1456	Second contact, aqueous (1459) with 40 v/o DEHPA	0.84	0.01	< D.L.	0.02	< D.L.	< D.L.	< D.L.
1457	Strip of 1456 organic with 150 gpl H_2SO_4	0.06	0.01	< D.L.	0.01	< D.L.	0.01	< D.L.

Notes:
- Starting solution treated for Fe, Cu, Zn removal before nickel testwork.
- Contact conditions: O/A = 1, Temperature = 25°C, time = 2-3 minutes.

TABLE 8.119. NICKEL EXTRACTION BY 40 v/o DEHPA - 70 GPL EHO

Sample No.	Final pH	Ni Concentration in Aqueous Phase (gpl)		Extraction (gpl)	Strip (gpl
		Initial	Final		
5056	3.1	4.37	2.97	32.0	100.0
5057	3.0	4.26	3.30	22.5	100.0
5058	2.7	5.10	3.84	24.7	100.0
5059	3.0	5.05	3.30	34.6	100.0
5060	3.0	5.31	2.92	45.0	100.0
				Average 31.8	

Notes: . O/A = 1 loading, O/A = 1 stripping, 50 cc each phase, 25^{o}C
. 200 gpl sulfuric acid

The change in order is not as important to the present project as the fact that the pH at which extraction occurs is shifted dramatically(44), Figure 8.25, i.e., the pH for 50% Ni extraction by D_2EHPA-EHO is 1.58 while the pH for 50% Ni extraction by D_2EHPA alone is 4.11. The D_2EHPA-EHO mixture appears to be worth further consideration as a means of concentrating the Ni content.

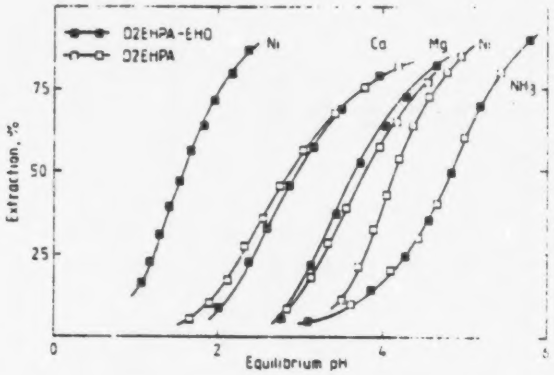


Figure 8.25. Extraction of nickel, calcium, magnesium by 0.5 M D_2EHPA and its mixture with 0.5 M 2-ethylhexanol oxime (EHO) (from Preston(43)).

A series of small scale shake tests were performed to verify that nickel could, indeed, be extracted from low pH solutions by a D_2EHPA-EHO mixture and a LIX63-D_2EHPA mixture. Also it was important to determine the selectivity of the organic for nickel in the presence of chromium.

A series of shake tests was performed at a pH of approximately three using the organic composition suggested in the study by Preston(44). The results shown an average extraction of approximately 32 percent nickel, Table 8.119.

A design matrix series was run and the results are reported in Table 8.120. Excellent extractions were achieved for several conditions, e.g., 80.2-83.1%, for a single contact. The stripping is also excellent. This system is far from being optimized. A graduate student is continuing the research beyond the results reported here. The system does appear to hold good potential for nickel recovery and concentration. If nickel could be solvent extracted from the chromium (+3) at a pH <2.5, then the expensive chromium

TABLE 8.120. DESIGN MATRIX FOR DEHPA - EHO SOLVENT EXTRACTION SYSTEM

Sample No.	Time (min)	EHO (gpl)	DEHPA (v/o)	pH(Final)	Concentration(gpl) Initial	Concentration(gpl) Final	Extraction (%)	Strip (%)
5061	3	70	20	1.20	3.01	1.76	41.5	100.0
5062	7	70	20	1.46	3.02	1.61	46.7	100.0
5063	3	130	20	1.41	3.02	0.98	67.5	71.6
5064	7	130	20	1.20	3.02	0.80	73.5	84.0
5065	3	70	60	1.41	3.01	1.39	53.8	100.0
5066	7	70	60	1.20	3.80	1.12	62.7	100.0
5067	3	130	60	1.15	3.29	0.65	80.2	100.0
5068	7	130	60	1.35	3.02	0.51	83.1	100.0
5069	7	130	60	1.34	3.02	0.55	81.8	100.0
5070	5	100	40	1.32	2.84	0.74	73.9	100.0
5071	5	100	40	1.31	3.00	0.74	75.3	100.0

Notes: . O/A = 1 for loading; O/A = 1 for stripping, 50cc each phase, 25oC
. 200 gpl sulfuric acid

oxidation would be unnecessary. The nickel could be extracted and recovered by electrowinning and the chromium could be precipitated as $Cr(OH)_3$; then calcined to Cr_2O_3. This system is presented as one of the cost alternatives in Section 8.15. A considerable saving in cost may be possible.

Another system has also been examined in a cursory manner; the LIX63-D_2EHPA system. An isotherm was run at a pH of 1.17 using a mixture of 12.5 v/o LIX63, 16.1 v/o D_2EHPA, remainder KERMAC 510. Good extraction is indicated by the data presented in Table 8.121. Chromium is not extracted. Testwork on both the above systems is continuing. Several variables will be investigated: the organic composition (EHO or LIX63 mixed with D_2EHPA); equilibrium pH; time of contact; temperature; stripping efficiency as a function of acid strength. Both systems appear to hold promise for nickel extraction at low pH levels.

8.12. FINAL LARGE SCALE SOLUTION PURIFICATION

A sample of the large scale test (sequential test series five) leach solution (after Fe, Cu, Zn, Cr and Ni removal) was treated by a cation exchange resin. The solution after nickel sulfide precipitation contained only 4 mg/l Cr and 6 mg/l Ni. All other elements were less than the analytical detection limit (<0.01 mg/l). A 150 cc sample was contacted with IRA-200, a strong cationic exchange resin in the hydrogen form and a second sample was contacted with the same type resin in the sodium form. The final Cr and Ni content was reduced to < 1 mg/l and 1 mg/l, respectively, using the H^+ form; and to 3 mg/l and 2 mg/l respectively using the Na^+ form.

Practically all of the final solution will be recycled to the leach unit operation, i.e., for the treatment of 100 pounds of sludge, most of the final solution volume will be recycled to satisfy the leach water requirement. Therefore, if IX is required as a final clean-up unit operation, it will be necessary to only treat a rather small volume of solution.

8.13. LARGE SCALE SEQUENTIAL METAL EXTRACTION AND RECOVERY TEST DATA

A series of large-scale tests were conducted to develop test data to design a particular unit operation; to design further testwork; or to verify

TABLE 8.121. NICKEL SOLVENT EXTRACTION BY LIX63 -DEHPA: ISOTHERM DATA SUMMARY

Sample No.	Condition	Concentration (gpl)					
		Ni	Cr	Cu	Fe	Zn	Pb
5071	Starting	5.544	10.525	0.022	0.007	0.020	0.002
5072	O/A = 10/1	0.695	10.728	0.007	0.005	0.004	0.013
5073	5/1	2.038	10.918	0.011	0.007	0.008	0.005
5074	2/1	3.325	10.669	0.040	0.007	0.007	0.022
5075	1/1	3.685	10.604	0.022	0.007	0.017	0.018
5076	1/5	4.368	10.529	0.013	0.008	0.014	0.010
5077	1/10	5.059	10.457	0.014	0.008	0.015	0.005

Notes: . Solution pH 1.17
. Organic: 12.5 v/o LIX 63, 16.1 v/o DEHPA, remainder KERMAC 510
. Temperature: 25^{o}C
. Time: 3 minutes

the applicability of a particular unit operation. These data are presented in the following tables and are referred to and discussed throughout the previous sections. The data are in a chronological order as collected. Not all unit operations were performed in every sequential test.

8.13.1. Sequential Test: Series One (83 Pound Test)

Purpose of test: Generate solutions for copper and zinc solvent extraction.

Results : Table 8.122, Sequential Test: Series One
Table 8.123, Sequential Test: Non-Recoverable Elements

Comments : First use of filter press resulted in the discovery that the diaphragm pump was not stainless steel as per specification. Pump contaminated filtered solution with iron. Test was not designed to collect mass balance data but was performed to gain experience with the large scale leach, filter press and SX equipment. Phase separations in the SX testwork were good, flowrate of solutions controllable, muck and crud formation minimal.

8.13.2. Sequential Test: Series Two (200 Pound Test)

Purpose of Test: A large leach was conducted then split into two volumes. One volume was saved to be used as stock solution for feeding into operating jarosite solution. The test objective was to investigate continuous jarosite precipitation under constant feed conditions. A second purpose was to prepare a large volume for SX work.

Results : Tables and 8.124, Sequential Test: Series Two
Table 8.123, Sequential Test: Non-Recoverable Elements

Comments : Continuous precipitation test not run because desired iron level in operating jarosite was not achieved. Zn SX did not remove all zinc in first series of contacts because insufficient D_2EHPA present. Zinc raffinate recycled through system twice more at higher starting pH levels. Gypsum precipitated in the strip cells.

8.13.3. Sequential Test: Series Three

Purpose of Test: Further large scale testwork on copper, zinc SX.

Results : Table 8.125, Sequential Test: Series Three
Table 8.123, Sequential Test: Non-Recoverable Elements

TABLE B.122. SEQUENTIAL TESTS: SERIES ONE (83 POUND TEST)

Sample No.	Conditions	Concentration (gpl)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
	Leach-Jarosite Precipitation							
1366	Leach solution, 53° C; (one-half hour, standard conditions); 64 liters	20.20 ↑ $[Fe^{++}$ = 0.91 gpl	5.15	8.04	1.08	13.96	0.77	2.23
1367	Leach solution, diluted and pH adjusted to 2.14, 90 liters	14.00	3.60	5.45	0.75	9.89	0.53	1.56
1371	Five hour exposure to potassium jarosite conditions. In-situ deposition of jarosite into leach residue. Sample after filtering through filter press. pH = 1.03 final. 90 liters of solution (later found to be iron contaminated by filter press pump)	4.02 ↑ $[Fe^{++}]$ = 0.92 gpl	3.62	6.32	0.65	11.38	0.62	1.77 (Vol.=78 lit.)
		Composition adjusted for solution loss from vessel						
		3.47	3.12	5.45	0.56	9.81	0.53	1.53
1440	Above solution (1371) pH adjusted with K OH to 2.75, volume 99 liters.	3.36	3.14	4.95	0.54	9.37	0.52	1.58
1466	Seven-hour exposure to potassium jarosite deposition. Filtered one-half batch before pump failed. pH final = 1.90 (see Note)	1.57	2.87	5.04	0.58	9.86	0.52	1.30 (Vol.=94 lit.)
		Composition adjusted for solution loss from vessel						
		1.49	2.72	4.79	0.55	9.36	0.49	1.23

TABLE 8.122. CONTINUED

Sample No.	Conditions	Concentration (gpl)						
		Fe	Cu	Ni	Cr	Zn	Cd	Al
	Copper SX (10 v/o LIX 622); Reister System; O/A = 1, 2-stage extraction; 1-stage strip (150 gpl H_2SO_4) recycled; 250 cc/min. flow rate							
1523	Solution 1466 diluted to ≈40 liters. Starting solution for Cu SX test (40 liters) Initial pH = 2.14	0.65	1.37	3.02	0.28	4.94	0.31	0.55
1524	Raffinate from contact. Final pH = 1.73, 40 liters	0.68	0.017	3.18	0.29	5.14	0.33	0.56
1526	Final strip solution; 3.8 l; (starting acid 150 gpl H_2SO_4); Note some solution carry over.	0.028	7.22	0.10	0.018	0.076	<D.L.	0.026
	Zinc SX (27 v/o DEHPA O/A = 1, 4-stage extraction; 2-stage strip (200 gpl H_2SO_4) recycled; 250 cc/min. flow rate., initial pH = 1.75, 40 liters of 1524							
1532	Raffinate from Contact, final pH = 1.29, 25 liters	0.46	0.014	2.84	0.25	1.00	0.28	0.32
1533	Final strip solution, 7.6 l; (starting acid 200gpl H_2SO_4)	0.005	<D.L.	0.018	0.004	4.74	0.016	0.035

TABLE 8.122. CONTINUED

NOTE:
- Barrel 4 sludge material. Sludge weight: 83.1 pounds. Solids weight: 27.4 pounds.
- Sludge Composition (%): Fe (14.2), Cu (3.73), Ni (4.60), Zn (8.87), Cr (0.72), Cd (0.48), Al (1.58).

- The filter press pump contaminated solution with iron. The iron content of solution before filtering was 0.068 gpl (68 ppm). After filtration the iron content was 1.44 gpl (sample 1466).
- LIX 622 loads copper that does not strip completely. This effect is characteristic of LIX.
- DEHPA concentration insufficient to remove all the zinc; DEHPA loads 0.15 gpl Zn per v/o DEHPA; therefore, 27 v/o DEHPA will extract only 4.0 gpl Zn. Also, later found that pH decreased in first two contacts to 1.3; therefore, last two stages of contact were not extracting Zn into the organic phase.
- Jarosite conditions: pH: 2-2.8, temperature: 88-92.

TABLE 8.123. SEQUENTIAL TEST: NON-RECOVERABLE ELEMENTS

Sample No.	Condition	Concentration (gpl)				
		Si	Ca	Al	Fe	P
	SERIES ONE (For condition details see Table 8.86)					
1366	Leach Solution	1.56	0.58	2.23	20.20	3.09
1367	Diluted	1.09	0.53	1.56	14.00	2.04
1371	5 hr Jarosite	1.16	0.60	1.77	4.02	1.48
1466	7 hr "	-	0.51	1.35	1.44	0.78
1523	Start for Cu SX	0.12	0.30	0.55	0.65	0.69
1524	Cu Raffinate (Also start for Zn SX)	0.12	0.31	0.56	0.68	0.16
1526	Cu Final Strip	0.03	0.06	0.03	0.03	3.17
1532	Zn Raffinate	0.11	0.17	0.32	0.46	0.17
1533	Zn Final Strip	0.01	0.13	0.03	0.01	<D.L.
	SERIES TWO (For condition details see Table 8.88)					
1765	Leach Solution	2.16	0.12	2.27	16.33	2.62
1757	1 hr Jarosite	1.78	0.13	1.87	2.87	1.03
1769	Final " (12 hr)	0.19	0.05	0.56	1.04	1.11
1802	Cu SX Feed	0.28	-	0.44	-	1.14
1816	Cu Raffinate	0.28	0.17	0.45	1.14	D.L
1817	Cu Final Strip	0.01	0.05	0.03	0.11	5.52
1811	Zn Feed(pH=1.75)	0.28	0.42	0.45	1.13	0.01
1824	Zn Raffinate,3.25 hrs.	0.27	0.02	0.28	1.00	0.01
1825	Zn Strip	0.03	0.21	0.17	D.L.	D.L.
1826	Zn Feed(pH=2.02)	0.27	0.13	0.29	0.97	0.02
1833	Zn Raffinate,2.75 hrs.	0.27	-	0.06	0.60	0.03
1834	Zn Strip	0.08	2.45	0.52	< D.L.	< D.L.
1882	Zn Feed(pH=2.5)	0.22	0.02	0.05	0.52	0.01
1889	Zn Raffinate,3 hr	0.22	0.18	D.L.	0.16	0.01
1890	Zn Strip	0.03	0.26	0.65	0.03	0.01

Continued

TABLE 8.123. CONTINUED

Sample No.	Condition	Concentration (gpl)				
		Si	Ca	Al	Fe	P
	SERIES THREE (For condition details see Table 8.89)					
1962	Final Jarosite Solution	1.15	0.80	2.99	0.46	1.09
1966	Large System Cu SX; Final raffinate after crud shutdown	1.16	2.48	0.44	0.44	0.92
1991	Small System Cu SX; leach solution diluted, starting solution.	0.68	0.54	1.58	0.28	1.08
2005	Cu Final Raff.	0.63	0.45	1.58	0.26	0.18
2066	Cu Final Strip	0.02	<D.L.	0.03	0.15	9.95
2005	Small System Zn SX; starting solution	0.63	0.45	1.58	0.26	0.22
2109	Zn Final Raff.	0.77	0.16	1.24	0.06	0.22
2110	Zn Final Strip	0.01	0.55	0.94	<D.L.	<D.L.
	SERIES FOUR (For condition details see Table 8.90)					
2116	Leach Solution	3.48	1.11	4.61	20.47	5.09
2118	Diluted leach	1.37	0.46	1.78	8.11	1.65
2126	Final Jarosite Treated Solution	1.47	0.58	1.78	0.34	1.12
2127	Cu SX Starting Solution	1.02	0.40	1.01	0.33	1.25
2144	Final Raff. 6 hr.	1.01	0.39	0.96	0.31	0.44
2143	Final Strip	0.12	<D.L.	<D.L.	0.05	31.08
2146	Cu SX Raff. after passing through system second time	0.98	0.38	0.93	0.29	0.20
2147	Final Strip, 6 hr	<D.L.	0.01	< D.L.	< D.L.	-

TABLE 8.123. CONTINUED

Sample No.	Condition	Concentration (gpl)				
		Si	Ca	Al	Fe	P
2177	Zn SX Starting Solution, pH = 2.0	0.88	0.40	1.22	0.29	0.02
2181	Final Raff, 2.5 hrs.	0.86	0.07	0.49	0.01	0.04
2180B	Final Strip	0.02	0.46	0.34	<D.L.	<D.L.
2242	Zn SX Starting Solution, pH = 3.0	0.16	0.32	0.81	0.58	0.02
2256	Final Raff, 6 hr	0.48	0.08	0.32	0.14	0.06
2181a	Chromium Oxid. starting solution before pH adjust	0.86	0.07	0.49	0.01	0.04
2361	pH adjusted to 5, aqueous phase	0.07	0.08	<D.L.	<0.01	<D.L.
2340	Chlorine oxid. 1 hr	0.07	0.10	0.02	0.01	<D.L.
2374	Chromium Reoxid. 1.5 hr.	0.03	0.07	0.01	<0.01	<D.L.
2376	Chromium Precip. by lead sulfate added to 2374	0.03	0.07	<0.01	<0.01	<D.L.
2348	Chromium Precip. #2, starting solution	0.05	0.09	<D.L.	<D.L.	<D.L.
2352	One hr exposure, 2X $PbSO_4$ added	0.05	0.09	<0.01	<D.L.	<D.L.
2364	Lead Sulfate-Lead Chromate	<D.L.	0.10	< D.L.	<D.L.	<D.L.
2367	Nickel Precip. from 10 liters of 2352, starting solution	0.04	0.04	< D.L.	<0.01	<D.L.
2378	Final Filtrate	0.03	0.04	< D.L.	< D.L.	< D.L.
SERIES FIVE (For condition details see Table 8.91)						
2492	Leach Solution	0.70	0.17	1.74	9.73	1.76
2494	Final Jarosite Solution	0.87	0.21	1.30	0.57	1.28

TABLE 8.123. CONTINUED

Sample No.	Condition	Concentration (gpl)				
		Si	Ca	Al	Fe	P
2494	Cu SX Starting Solution	0.87	0.21	1.30	0.57	1.28
2499	Final Raff.	0.82	0.22	1.25	0.52	1.28
2500B	Final Strip	D.L.	0.03	< D.L.	< D.L.	7.72
2525	Zn SX Starting Solution, pH = 2.0	0.82	0.22	1.20	0.37	0.18
2526A	Final Raff.for starting pH = 2.0	0.79	0.07	0.40	0.16	0.19
2524	Final Raff. for starting pH = 2.5	0.51	0.04	0.52	0.07	0.20
2526B	Composite Raff.	0.75	0.04	0.38	0.18	0.21
2527	Final Strip	0.09	0.49	8.27	< D.L.	< D.L.
2564	Chromium Oxid. starting solution	0.86	0.04	0.39	0.22	0.17
2592	Final Oxid. solution, 83.6% oxidized	0.24	0.05	0.08	< D.L.	< D.L.
2600	Chromium Precip.	0.27	0.04	0.16	0.03	< D.L.
2603	Final Exposed Solution, 45 min.	0.17	0.04	0.14	D.L.	< 0.01
2605	NiS Precipitation starting solution	0.23	0.03	< 0.01	< D.L.	< D.L.
2610	Final exposed solution, 60 min.	0.19	0.03	< D.L.	< D.L.	< D.L.

TABLE B.124. SEQUENTIAL TEST: SERIES TWO (200 POUND TEST)

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Zn	Cr	Ni	Cd	Al
	Leach-Jarosite Precipitation							
1765	Starting Solution, one-half hour standard leach; about one half of leach solution subjected to jarosite conditions, 60 liters	16.33	1.48	9.96	1.05	8.47	0.46	2.27
1757	One hour exposure	2.87	1.08	8.57	0.69	7.12	0.39	1.87
1769	Twelve hour exposure. pH overshot drastically	1.04	1.04	8.31	0.55	6.94	0.38	1.68
1802	Final solution after filtration, pH adjusted to 1.9.	1.13	0.39	8.89	0.26	8.02	0.41	0.44
	Copper SX							
1802	Feed Solution as above							
	Copper Raffinate (Starting pH=1.9)							
1797	1/2 hour	1.12	0.007	8.89	0.26	7.87	0.41	0.45
1799	1 hour	1.13	0.014	8.89	0.26	7.99	0.41	0.45
1805	2 hours	1.14	0.065	8.89	0.26	8.00	0.41	0.45
1809	3 hours	1.16	0.071	8.91	0.27	8.22	0.43	0.46
1816	4 hours	1.14	0.022	8.84	0.27	8.07	0.42	0.45

TABLE 8.124. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Zn	Cr	Ni	Cd	Al
	Zn SX (Feed from Cu SX adjusted to pH = 1.75)							
1811	Feed Composition	1.13	0.058	8.84	0.27	8.02	0.42	0.45
1814	1.5 hours	0.97	0.051	1.79	0.27	8.06	0.40	0.27
1818	2.5 hours	0.93	0.034	1.67	0.25	7.65	0.38	0.26
1824	3.25 hours	1.00	<D. L.	1.63	0.27	8.08	0.47	0.28
	Above Raffinate Adjusted to pH = 2.02 and Recycled through System							
1826	pH Adjusted Feed	0.97	0.005	1.63	0.27	8.10	0.41	0.29
1827	1 hour	0.60	<D. L.	0.09	0.26	7.99	0.29	0.06
1831	2 hours	0.59	0.011	0.55	0.26	8.45	0.35	0.06
1833	2.75 hours	0.60	0.013	0.58	0.27	8.67	0.37	0.06
	Above Raffinate Adjusted to pH = 2.50 and Recycled through System							
1882	Feed	0.60	0.013	0.58	0.27	8.67	0.37	0.06
1885	1 hour	0.12	0.002	<D. L.	0.25	8.25	0.17	0.004
1889	3 hours			<D. L.	0.25	8.17	0.13	<D. L.

NOTE: Starting Sludge Composition (average of 7 samples in %): 18.69 ± 1.35 Fe, 10.11 ± 1.54 Zn, 1.07 ± 0.03 Cr, 8.52 ± 0.73 Ni, 2.25 ± 0.28 Al, 0.43 ± 0.03 Cd
Barrel 14 sludge; 81.6% H_2O; 18.6% solids.

TABLE 8.124. CONTINUED

- Leach-Jarosite
  - Standard leach conditions, 156 liters
  - Standard jarosite conditions initially established. pH overshot during las two hours of test. Significant metal value lost by hydroxide precipitation.
- Cu SX
  - Two stages of contact (initial pH = 1.90, 1 stage of scrub (100 gpl K_2SO_4), 1 stage of strip (175 gpl H_2SO_4, aqueous solution recycled).
  - O/A = 1, 10 v/o LIX 622, 90 v/o KERMAC 470B.
  - Organic previously used and not retreated before this application.
- Zn SX
  - Four stages of contact (O/A = 2), two stages of strip (O/A = 2, 200 gpl H_2SO_4 fresh solution).
  - 40 v/o DEHPA, 60 v/o KERMAC 470B.
  - Strip solution recycled.
  - Feed rate 0.25 l/min for organic and aqueous.

TABLE 8.125. SEQUENTIAL TESTS: SERIES THREE (75 POUND TEST)

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Zn	Cr	Ni	Cd	Al
	Residue-Jarosite Precipitation							
1961	Final 6 hour exposure, 82 lit.	0.50	4.07	10.55	0.72	5.61	0.58	3.07
1962	Final solution allowed to settle 8 hours	0.46	3.99	10.24	0.70	5.36	0.56	2.99
	Large System Cu SX							
	10 v/o LIX 622, 90 v/o KERMAC 470B; two stages of K_2SO_4 (100 gpl) scrub; two stages of strip (150 gpl H_2SO_4); aqueous phase initial pH ≅ 2.0. System uncontrollable because of crud formation.							
	Small System Cu SX							
	Above leach solution diluted to increase available volume of solution; two stages of kerosene scrub; two stages of contact (O/A = 1); two stages of strip (O/A = 1).							
1991	Starting feed solution	0.28	2.32	5.96	0.42	3.78	0.41	1.58
2005	Final raffinate, approximately 20 lit. run through system.	0.26	0.047	5.70	0.40	3.39	0.36	1.58
2006	Final strip	0.15	28.71	0.10	0.008	0.04	< D.L.	0.03

TABLE 8.125. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Fe	Cu	Zn	Cr	Ni	Cd	Al
	Small System Zn SX							
	Four stages of contact; pH adjustment after first two stage; three stages of strip.							
2005	Starting Solution	0.26	0.05	5.70	0.40	3.39	0.36	1.50
2096	Raff. from stage two, 3 hrs	0.08	0.04	0.72	0.39	3.04	0.44	1.60
2097	Raff. from stage four, 3 hrs	0.03	0.04	0.03	0.38	3.02	0.44	1.60
2098	Strip, 3 hrs	0.01	0.02	26.30	0.01	0.08	0.16	0.51
2100	Raff. from stage two, 4 hrs	0.08	0.04	0.66	0.39	3.05	0.46	1.59
2102	Raff. from stage four, 4 hrs	0.04	0.04	0.04	0.38	3.00	0.32	0.82
2104	Strip, 4 hrs	< D.L.	0.01	28.71	0.01	0.11	0.17	0.57
2108	Raff. from stage two, 7 hrs	0.10	0.04	1.24	0.39	3.15	0.38	1.80
2109	Raff. from stage four, 7 hrs Approximately 20 lit.	0.06	0.03	0.15	0.41	3.26	0.34	1.24
2110	Strip, 7 hrs	< D.L.	0.02	33.05	< 0.01	0.11	0.18	0.84

Notes:
- Sludge from barrels 2 and 4 mixed. 75# sludge, 21.8# solids.
- Standard leach conditions
- Standard jarosite conditions.
- Large: Cu SX
  - Two stages of extraction, O/A =1; Two stages of scrub, 100 gpl K_2SO_4, O/A =1; Two stages of strip, 150 gpl H_2SO_4, O/A = 1, recycled strip.
  - Solution flowrate, 250 cc/min, temperature, 35-45°C.
- Small: Cu SX
  - Two stages of extraction, O/A = 1; 10 v/o LIX 622 (from large cells); Two stages of kerosene scrub, O/A = 1; Two stages of strip, 150 gpl acid, O/A = 1.
  - Solution flowrate, 50 cc/min, temperature 35-45°C.

TABLE 8.125. CONTINUED

Notes: . Small: Zn SX

- Four stages of extraction, O/A = 1; 40 v/o DEHPA; pH adjusted to 2.0 after first two stages; flowrate 50 cc/min, temperature 55^{0}C.
- Three stages of strip; O/A = 1; recycled strip acid; 200 gpl H_2SO_4(initial)

Comme : Leach and jarosite precipitation went very well. Lowered iron content from 14.49 gpl Fe to 500 ppm in six hours. Cu SX completely uncontrollable; a great deal of crud formed and the test had to be terminated. The suspected problem was K_2SO_4 scrub stages. SEM work (Figure 8.26) showed large amounts of potassium and sulfur in the crud material. Testwork performed on small Bell system to determine problem. Problem was overagitation in the mixer cells. This problem was overcome by adding flowmeters to each mixer cell so that an even flow was established to each cell.

Small scale zinc tests were conducted to study pH readjustment after two stages of contact. Results were favorable. Gypsum formed in strip cells. A filter system was devised.

8.13.4. Sequential Test: Series Four (35 pound test)

Purpose of Test: To produce a solution (containing 20 gpl Fe) to carry completely through the flowsheet.

Results : Table 8.126, Sequential Test: Series Four
Table 8.123, Sequential Test: Non-Recoverable Elements

Comments : Copper SX problem described in Sequential Test three overcome by better control of mixer agitation and removal of K_2SO_4 strip cells. LIX-622 content insufficient for complete copper removal in this continuous test so solution cycled through system again.

Thirty liters of chromium-nickel solution treated as depicted below:

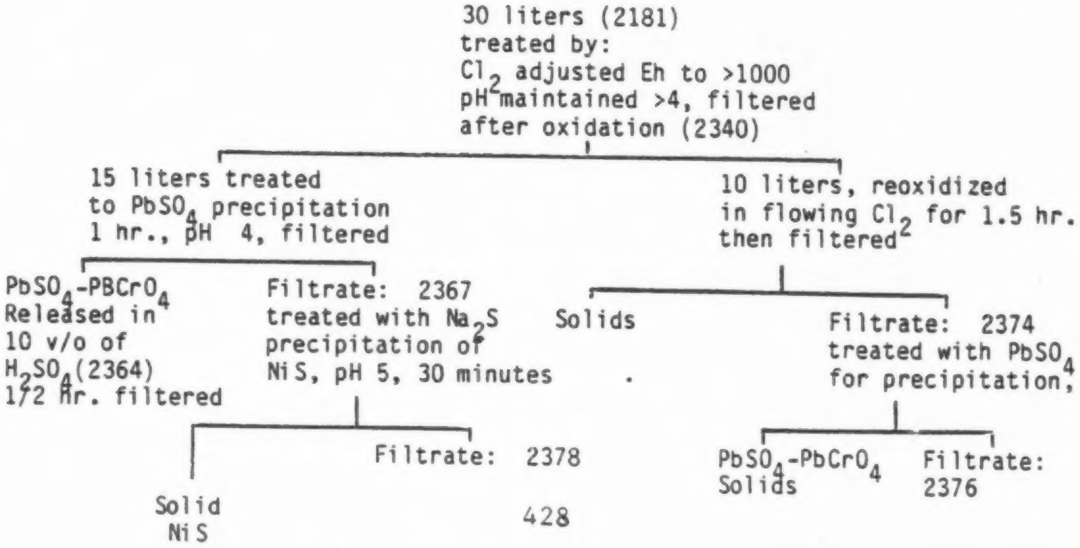

30 liters (2181) treated by: Cl_2 adjusted Eh to >1000 pH maintained >4, filtered after oxidation (2340)
15 liters treated to $PbSO_4$ precipitation 1 hr., pH 4, filtered
10 liters, reoxidized in flowing Cl_2 for 1.5 hr. then filtered
$PbSO_4$-$PBCrO_4$ Released in 10 v/o of H_2SO_4 (2364) 1/2 hr. filtered
Filtrate: 2367 treated with Na_2S precipitation of NiS, pH 5, 30 minutes
Solids
Filtrate: 2374 treated with $PbSO_4$ for precipitation,
Solid NiS
Filtrate: 2378
$PbSO_4$-$PbCrO_4$ Solids
Filtrate: 2376

TABLE 8.126. SEQUENTIAL TESTS: SERIES FOUR (35 POUND TEST)

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
	Standard Leach (Barrel 1), 30 liters							
2114	15 minutes	11.15	20.37	17.70	1.75	7.99	1.13	4.50
2115	30 minutes	11.16	20.24	17.67	1.74	8.01	1.12	4.51
2116	45 minutes	11.16	20.47	18.04	1.76	7.96	1.14	4.61
	Jarosite							
2118	Leach Solution Diluted, 60 lit;	5.21	8.11	7.12	0.70	3.14	0.44	1.78
2119	1 hour jarosite, 57 lit.	5.14	0.92	7.55	0.53	3.30	0.46	1.68
		Adjusted composition for solution volume decrease.						
		4.88	0.87	7.17	0.50	3.14	0.44	1.60
2125	6 hour jarosite, 51 lit.	5.49	0.33	8.00	0.48	3.71	0.51	1.69
		Adjusted composition for volume decrease						
		4.66	0.28	6.80	0.40	3.15	0.43	1.51
2126	Jarosite settled from solution (8 hours), 47 lit.	5.81	0.39	8.58	0.52	3.91	0.55	1.79
		Adjusted composition for volume decrease						
		4.55	0.30	6.72	0.41	3.06	0.43	1.40
	Cu SX (10 v/o LIX 622), 90 lit.							
2127	Solution diluted, pH = 2.01	3.89	0.33	5.80	0.36	3.15	0.44	1.01
2129	Raffinate, 2 hours (pH = 1.38)	0.38	0.31	5.63	0.35	3.06	0.42	0.98
2130	Strip, 2 hours	6.80	0.01	<0.01	<0.01	<D. L.	<D. L.	0.06
2132	Strip, 3.5 hours	7.87	0.01	<0.01	<0.01	<D. L.	<D. L.	0.02
2133	Raffinate, 5 hours (pH = 1.40)	1.18	0.32	5.72	0.35	3.14	0.44	0.99

TABLE 8.126. CONTINUED

Sample No.	Condition	Concentration (gpl)							
		Cu	Fe	Zn	Cr	Ni	Cd	Al	
2134	Strip, 5 hours	37.46	0.01	0.11	0.04	<D.L.	<D.L.	<D.L.	
2142	Final Raffinate, 6 hrs.	1.34	0.30	3.42	0.33	3.07	0.42	0.93	
2144	Final Composite Raffinate	0.78	0.31	5.58	0.34	3.20	0.44	0.96	
2143	Final Composite Strip	42.31	0.05	0.14	0.04	0.03	<D.L.	<D.L.	
	Recycled (2144) through system								
2145	Final Raffinate, 6 hrs, 75 l	0.109	0.29	5.46	0.32	3.08	0.42	0.92	
2146	Final Composite Raffinate	0.116	0.29	0.33	0.33	3.13	0.43	0.93	
2147	Final Composite Strip, 6 hrs. (new acid at start)	---	<D.L.	<D.L.	0.02	0.01	<D.L.	<D.L.	
	Zn SX (40 v/o DEHPA), 50 liters								
2177	Starting Solution, pH adjusted to 2.0	0.09	0.29	5.89	0.37	2.56	0.32	1.22	
2178	Raffinate after Second Contact, 1 hr.	0.09	0.06	1.77	0.35	2.56	0.34	0.86	
2179	Raffinate after Fourth Contact, 1 hr.	0.08	0.02	0.15	0.34	2.44	0.22	0.53	
2181	Final Composite Raffinate	0.08	0.01	0.13	0.37	2.54	0.24	0.49	$SO_4^=$
2180B	Final Composite Strip	<0.01	<D. L.	21.85	0.02	0.05	0.04	0.34	199.6
	Zn SX (40 v/o DEHPA)								
	Same system set-up and solutions as above but a different leach solution (2092) used.								

TABLE 8.126. CONTINUED

Sample No.	Condition	(Concentration (gpl)) Cu	[illegible]	Zn	Cr	Ni	Cd	Al
2242	Starting Solution pH Adjusted to 3.0	0.11	0.58	4.94	0.26	2.69	0.27	0.81
2243	Raffinate After Second Contact, Start	0.11	0.39	0.48	0.27	2.72	0.37	0.58
2244	Raffinate After Fourth Contact, Start	0.09	0.02	0.05	0.35	2.61	0.28	0.33
2245	Strip, Start	0.02	<D.L.	25.59	0.01	0.04	0.11	0.40
2246	Raffinate After Second Contact, 1 hr.	0.11	0.39	0.33	0.26	2.71	0.35	0.54
2247	Raffinate After Fourth Contact, 1 hr.	0.10	0.19	0.04	0.28	2.72	0.27	0.34
2248	Strip, 1 hr.	0.02	<0.01	34.43	0.02	0.06	0.15	0.61
2250	Raffinate After Second Contact, 2 hrs.	0.11	0.40	0.23	0.28	2.90	0.37	0.42
2251	Raffinate After Fourth Contact, 2 hrs.	0.10	0.20	0.04	0.25	2.74	0.27	0.27
2252	Strip, 2 hrs	0.03	<D.L.	38.99	0.02	0.05	0.16	0.76
2253	Raffinate After Second Contact, 3 hrs.	0.12	0.39	0.24	0.26	2.87	0.36	0.46
2254	Raffinate After Fourth Contact, 3 hrs.	0.11	0.20	0.05	0.26	2.84	0.29	0.22
2255	Strip, 3 hrs.	0.04	<D.L.	42.83	0.01	0.07	0.19	0.91
2256	Final Raffinate, 6 hrs.; 90 liters	0.10	0.14	0.06	0.31	2.78	0.30	0.32
	Chromium Slurry Oxidation (Eh maintained)							
2181a (Before pH adjust)	30 liters of solution (pH = 1.3, Eh = 380 mv) 2181 doped with 42 gpl	0.08	0.01	0.13	1.69	2.54	0.24	0.49

TABLE 8.126. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
	Cr^{+++} solution then raised in pH to 5, Eh to >1000 mv with Cl_2, pH maintained >4 and Eh near 1000							
2361	Starting Solution adjusted to pH = 5, filtered aqueous sample (most of chromium in solids)	<D.L.	0.001	<D.L.	0.27	1.75	0.23	<D.L.
2340	One Hour Sample, exposed only periodically to Cl_2, Eh maintained at 1000 mv and pH >4, filtered aqueous sample (time to 2 hrs. showed no improvement in Cr oxidation)	0.04	0.01	0.08	1.15 (42% oxidized)	2.14	0.25	0.02
	Chromium Slurry Oxidation							
	3.5 liters of above oxidized slurry reoxidized by constant exposure to Cl_2							
2371	Starting Slurry, filtered, aqueous sample analyzed	0.02	<D.L.	0.08	0.66	2.24	0.27	<D.L.

TABLE 8.126. CONTINUED

Sample No.	Condition	Concentration (gpl)								
		Cu	Fe	Zn	Cr	Ni	Cd	Al	Cl^-	$SO_4^=$
2372	Thirty minute exposure to Cl_2, filtered sample	0.05	<0.01	0.09	1.36	2.37	0.28	0.01		
2373	One hour exposure to to Cl_2, filtered sample	0.06	<0.01	0.11	1.59	2.49	0.28	0.01		
2347	One and one-half hour exposure to Cl_2, filtered sample, most solids in solution, final filtrate	0.07	<0.01	0.11	1.65 (>95% oxidized)	2.31	0.24	0.01	0.54	23.73
	Chromium Precipitation									
	Lead sulfate (2X stoichiometric requirement) added to solution 2374 to precipitate $PbCrO_4$, pH maintained at 4, 10 liters									
2375	Thirty minute exposure	0.07	<D.L.	0.11	0.009	2.11	0.22	<0.01		
2376	Final Filtrate	0.06	<0.01	0.10	0.008	2.03	0.21	<0.01		
	Chromium Precipitation #2									
	15 liters of solution 2340 (only 42 % oxidized) exposed to lead sulfate without reoxidizing.									

TABLE 8.126. CONTINUED

2348	Starting Aqueous Solution; pH adjusted to 4.0	0.02	< D.L.	0.08	0.73	2.31	0.28	< D.L.
2349	One-half hr exposure	0.02	< 0.001	0.08	0.56	2.32	0.28	< 0.001
2352	One hr exposure	0.02	< D.L.	0.08	0.17	2.31	0.28	< D.L.
2364	Lead Chromate-Lead Sulfate Residue washed, dried, redissolved in 10 v/o acid; 46.4 g leached in 100cc solution.	< D.L.	< D.L.	< D.L.	7.51	0.008	0.04	< D.L.
	Nickel Precipitation							
	Na_2S added as a solution over a period of 20-30 minutes, maintaining pH = 5; approximately stoichiometric amount of Na_2S added to 10 liters							
2367	Starting Solution(2352 not 2376) ; Initial pH = 3.7	0.02	< 0.01	0.07	0.16	2.27	0.26	< D.L.
2378	Final Filtrate (Cl- = 2.61 gpl, $SO_4^=$ = 28.23 gpl)	< D.L.	< D.L.	< D.L.	0.04	0.07	< D.L.	< D.L.

NOTE: ·Barrel 1 sludge composition (34.40% solids, 65.6% H_2O): 7.8 Cu; 18.3 Fe; 11.5 Zn; 1.2 Cr; 5.5 Ni; 2.8 Al

·Standard leach on 35.58 pounds of sludge (55°C); final volume 29.6 liters of 20 gpl Fe; diluted to 57.6 liters, pH = 1.9.

·Conditions changed to precipitate potassium jarosite; temperature adjusted to 90°C; pH to 2.45; 1 gm K_2SO_4/gm Fe, 6 hours.

·Jarosite solution set 8 hours (overnight) then solution decanted off; residue diluted then filtered in filter press.

TABLE 8.126 CONTINUED

- Jarosite solution diluted to decrease Zn content to design range; total volume approximately 90 liters.

- Cu SX: LIX 622 (10 v/o); 2 stages of extraction (O/A = 1); 2 stages of strip (150 gpl H_2SO_4 (O/A =1), flow rate 250 cc/min., initialpH = 2.0, final raffinate pH = 1.3, temperature 30-40°C. Contacts performed in 1 gal. mixer-1 gal. settler system.

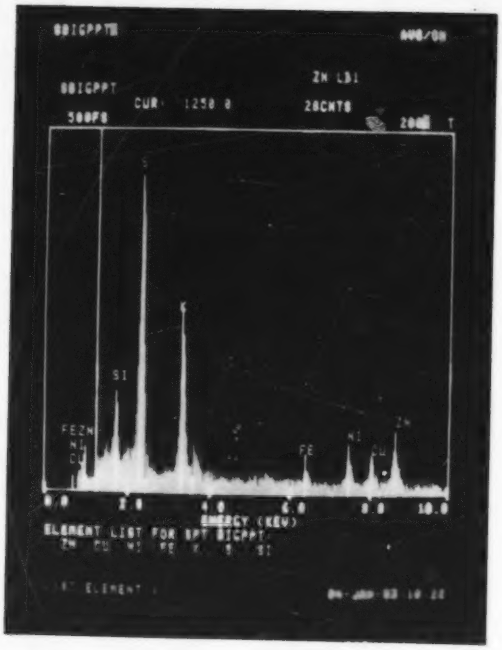
- Zn SX: DEHPA (40 v/o); 4 stages of extraction (O/A = 1); pH adjusted after first two contacts back to pH = 2; 3 stages of strip (200 gpl H_2SO_4, O/A = 1); temperature 30-40°C; initial pH = 2.0, final raffinate pH = 1.3.

- Zn SX: DEHPA (40%) test repeated at initial pH = 3; readjusted pH after second contact to pH = 2. Aqueous solution from previous test (90 liters) used. Otherwise, conditions same as above.

- Cr oxidation by Eh control tried on 30 liters of solution. Results required reoxidation. 10 liters. of slurry reoxidized in flowing Cl_2 (0.2 l/min.) while pH maintained greater than 4.

- $PbSO_4$ used as precipitating agent for chromium removal as $PbCrO_4$. $PbCrO_4$ can be redissolved to form chromic acid and lead sulfate regenerated for reuse. Very effective precipitant and easily filtered.

- Na_2S used as nickel precipitant. Very rapid precipitation but pH must be maintained near 5; if lower H_2S odor results, if much higher then nickel precipitates as $Ni(OH)_2$.



Elements Present: Si, Fe, K, Cr, Ni, Cu, Zn, S, P.

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Figure 8.26. Sequential test series three crud: qualitative analysis.

8.13.5. Sequential Test: Series Five (111 pound test)

Purpose of Test: Large Scale leach to carry out all unit operations.

Results : Table 8.127, Sequential Test: Series Five
Table 8.123, Sequential Test: Non Recoverable Elements
Table 8.128, Reagent Consumption for the Treatment of 50.6 kg (111 pounds) of Metal Finishing Hydroxide Sludge
Table 8.129, Acid Leach of Residue - Jarosite Solids: Sequential Series Five
Table 8.130, Toxicity Test Applied to Releached Jarosite Product from Sequential Test Five

Comments : The entire sequence of operations went well:

The large leach system easily handles 100 pounds of sludge material. The solid-liquid ratio can be varied to produce a solution that contains between 10-15 gpl Fe. This iron level is required for production of an easily filterable jarosite-residue mixture.

The jarosite in-situ precipitation produces a solid that settles rapidly. Therefore, most of the solution can be decanted from the solids. The slurry remaining can be conveniently handled in the LASTA filter press. Iron content can be decreased in the mixed metal solution to 0.5-1.0 gpl. This level is appropriate and can be removed during Zn SX. The exit pH from jarosite treatment is at a convenient level for Cu SX.

The sequential five test showed high copper loss to the residue-jarosite solids because of two reasons; the pH of the leach was high so copper leached into solution was lower than usual and the pH of the jarosite precipitation was also higher than normal; $\sim$2.9 which meant that some copper was precipitated. A leach of the residue-jarosite solids showed recovery of 75% of the copper; Table 8.129.

Copper solent extraction in the Reister System operates well. Interfaces are controllable and very little crud forms. That which does form can be siphoned off. Copper contents can be handled up to at least 10 gpl. Fifteen to twenty-seven liters/hr. can be treated.

TABLE 8.127. SEQUENTIAL TESTS: SERIES FIVE (111.6 POUND TEST)

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
2492	Standard Leach (Barrel 18) 212 liters	3.25	9.73	5.27	3.92	1.21	0.08	1.74
	Jarosite Precipitation							
2493	One hr exposure, 211 lit.	2.29	2.42	5.29	3.29	1.31	0.08	1.52
2494	Seven hr exposure, 200 lit. Final pH = 1.91	3.05	0.57	5.58	3.08	1.67	0.11	1.30
	Cu SX (15 v/o LIX 622)							
2494	Starting Solution, Initial pH = 1.91, 160 liters.	3.05	0.57	5.58	3.08	1.67	0.11	1.30
2496	Raffinate, 2 hrs	0.01	0.55	6.48	3.03	1.63	0.10	1.27
2499	Final Composite Raffinate Final pH = 1.3	0.03	0.52	6.47	2.95	1.68	0.10	1.25
2500B	Final Strip	23.17	< D.L.	0.06	0.08	0.04	< D.L.	< D.L.
	Zn SX (40 v/o DEHPA)							
2525	Starting Solution, pH = 2.	0.04	0.37	6.20	2.79	1.77	0.14	1.20
2526A	Raff. after stage 2, Initial pH = 2; 160 liters.	0.04	0.16	0.07	2.72	1.72	0.17	0.40
2524	Raff. after stage 4, Initial pH = 2.5	0.02	0.07	0.08	2.57	2.22	0.13	0.52
2526B	Composite Raff. (Final pH = 1.3; Cl^- = 1.36 gpl; $SO_4^=$ = 46.8 gpl)	0.04	0.13	0.07	2.55	1.78	0.13	0.38
2527	Final Strip Acid (Cl^- = 0.68 gpl; $SO_4^=$ = 90.3 gpl)	0.03	<D.L.	67.35	0.32	0.26	0.06	8.27

TABLE 8.127. CONTINUED

Sample No.	Condition	Composition (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
	Chromium Slurry Oxidation							
2564	Starting Solution, 75 lit., Eh = 350 mv, pH = 1.30	0.04	0.22	0.07	2.67	1.75	0.11	0.39
2574	Two hr exposure to chlorine, Eh = 888 mv, pH = 4.38	0.03	0.08	0.05	1.70 (52.6% of the chromium oxid.)	1.45	0.09	0.19
2580	Two and one-half hr exposuse; Eh = 1005 mv, pH = 4.2	0.03	0.12	0.06	2.02 (66.8% oxid.)	1.58	0.10	0.26
2589	Four hr exposure; Eh = 1138 mv, pH = 4.0	0.02	D.L.	0.05	2.25 (82.5% oxid.)	1.76	0.11	0.03
2592	Five hr exposure, Eh = 1132 mv, pH = 4.2 (Cl^- = 12.6 gpl; $SO_4^=$ = 33.9)	0.03	D.L.	0.06	2.28 (83.6% oxid.)	1.68	0.11	0.08
2638	Leach of solids from oxidation; 4.98 g in 100cc of 10 v/o H_2SO_4	0.004	3.21	< D.L.	0.57	0.11	< D.L.	0.80
	Chromium Precipitation							
	Lead sulfate added to 42 liters of 2592 solution							
2600	Starting Solution, 42 liters, pH = 4.2	0.03	0.03	0.06	2.34	1.57	0.10	0.16
2601	Solution pH adjusted to 4.7; approx. 1X stoichiometric lead sulfate added (558 g), exposure 5 min.	0.03	< D.L.	0.06	0.80	1.60	0.10	0.09
2602	Thirty min. exposure, 2X $PbSO_4$; Eh = 1090 mv; pH = 3.8	0.03	< D.L.	0.07	0.007	1.62	0.10	0.14
2603	Forty min. exposure, Eh = 1031 mv, pH = 4.5; (Cl^- = 6.8 gpl; $SO_4^=$ = 21.0)	0.03	< D.L.	0.06	0.007	1.59	0.11	0.14

TABLE 8.127. CONTINUED

Sample No.	Condition	Concentration (gpl)						
		Cu	Fe	Zn	Cr	Ni	Cd	Al
	Lead Sulfate-Lead Chromate Releach							
2640	Leach of solids, 50g solids in 100cc 20 v/o H_2SO_4	< D.L.	0.15	< D.L.	30.77	< D.L.	0.01	0.23
2641	Wash of solids from 2640 (154 cc)	< D.L.	0.07	< D.L.	5.27	< D.L.	< D.L.	0.10
2643	Wash of solids from 2640 (458 cc)	< D.L.	0.002	< D.L.	0.47	< D.L.	< D.L.	< D.L.
	NiS Precipitation							
	Na_2S added (2X stoichiometric addition as solution, 325 gpl) to solution slowly over 45 minute period, pH maintained between 4-5.							
2605	Starting Solution 2603	0.04	< D.L.	0.06	0.01	1.67	0.10	0.10
2606	Ten min. exposure	< D.L.	"	"	"	1.53	< D.L.	"
2607	Twenty min. exposure	"	"	"	0.007	0.02	"	"
2609	Forty-five min. exposure, Na_2S addition complete.	"	"	"	0.005	0.005	"	"
2610	Sixty min. exposure	"	"	"	0.004	0.006	"	"
	Ion Exchange of Final Solution							
2644	NiS filtrate, feed to column; IRA-200, 150 cc	< 0.001	0.20	< D.L.	0.002	< D.L.	< D.L.	< D.L.
2645	IX of 2644 (H^+ form)	"	0.001	"	< 0.001	"	"	"
2646	IX of 2644 (Na^+ form)	"	0.034	< D.L.	0.003	0.002	"	"

Notes: . Sludge barrel 18. Composition (%): 5.86 Cu, 17.71 Fe, 8.31 Zn, 6.09 Cr, 2.27 Ni, 0.09 Cd, 2.79 Al, 0.50 Ca; 26.3 % solids.

TABLE 8.127. CONTINUED

- **Leach**
  Sludge leached to produce an iron content of approximately 10 gpl, standard conditions.

- **Jarosite**
  Standard conditions: 88-92°C, pH = 2.2-2.7, 1 g K_2SO_4/g Fe, 7 hours. Solution slurry set overnight then solution decanted off, residue diluted then filtered in filter press. Solids subjected to EP test.

- **Cu SX**
  LIX 622 (15 v/o); 2 stages of extraction, O/A = 1; 2 stages of strip, 150 gpl H_2SO_4; O/A = 1; temperature 40 - 50°C; flowrate 250 cc/min each phase; initial pH = 1.9; contacts performed in Reister system.

- **Zn SX**
  DEHPA (40 v/o); 4 stages of extraction, O/A = 1; pH adjusted after first two contacts to 2.5; 3 stages of strip, 200 gpl H_2SO_4, O/A = 1, temperature 30-40°C; initial pH = 2.0; final raffinate pH = 1.3.

- **Chromium Slurry Oxidation**
  pH maintained between 4-5; chlorine sparged into vessel at 5 liters/min; Eh >1000mv; system agitated to suspend solids in solution. Degree of chromium oxidation determined by filtering sample, exposing solution to IRA 900 anionic exchange resin to remove oxidized chromium species; degree of oxidation calculated by difference.

- **Chromium Precipitation**
  Lead sulfate (≈2X stoichiometric requirement) added to agitated solution. PH≈ 4 maintained. Lead chromate solids filtered easily.

- **NiS Precipitation**
  Sodium sulfide solution (325 gpl) added slowly to solution over a period of 45 min.; Solution agitated to suspent particles; pH = 4-5. No odor problem.

- **Ion Exchange**
  Most of the final solution can be recycled as make-up water.

TABLE 8.128. REAGENT CONSUMPTION REQUIRED FOR THE TREATMENT OF 50.6 KG (111.6 POUNDS) OF METAL FINISHING HYDROXIDE SLUDGE

Unit Operation	Reagent	Amount
Leach	H_2SO_4	13.3 Kg (Concentrated acid)
	H_2O	12 liters new water 156 liters recycle water
Jarosite Precipitation	KOH	10 liters (500 gpl)
	H_2O_2	2.5 liters (30 v/o)
Filter Press	H_2O	14 liters
Solvent Extraction		
Copper	LIX 622	1.2 liters (one time addition)
	KERMAC 470B	6.8 liters " " "
	H_2SO_4	8 liters (Recycle acid 150 gpl)
Zinc	D_2EHPA	10.8 liters (one time addition)
	KERMAC 470B	16.2 liters (" " "
	H_2SO_4	11 liters (Recycle acid, 200 gpl)
	HCl	4 liters (4N)
Chromium Oxidation		
Chlorine	NaOH	8 liters (500 gpl)
	Cl_2	Not established
Electrochemical	H_2SO_4	Regenerates acid
Chromium Precipitation	NaOH	1 liter (400 gpl)
	$PbSO_4$	4.2 Kg (one time addition)
Nickel Precipitation	Na_2S	6 liters (325 gpl)
	H_2SO_4	1 liter (200 gpl)

TABLE 8.129. ACID LEACH OF RESIDUE-JAROSITE SOLIDS: SEQUENTIAL SERIES FIVE, VARIABLE PH

Sample No.	Condition	Recovery From Solids(%)						
		Fe	Cu	Zn	Cr	Ni	Cd	Al
2698	Initial pH = 0.5	11.5	75.0	66.7	18.8	100.0	< D.L.	13.3
2701	Initial pH = 1.5	5.9	25.0	33.3	1.2	0.0	< D.L.	2.0
2702	Initial pH = 2.5	0.2	7.1	10.0	0.3	0.0	< D.L.	0.0

Notes:
- . 10 grams solid slurried in 100 cc solution, pH adjusted to desired value; ambient temperature, 18 hours.
- . Solid starting composition (%): 19.8 Fe, 2.8 Cu, 0.28 Zn, 3.2 Cr, 0.04 Ni, 0.0 Cd, 1.5 Al

TABLE 8.130. TOXICITY TEST APPLIED TO RELEACHED JAROSITE PRODUCT FROM SEQUENTIAL TEST FIVE

Sample No.	Condition	Concentration (mg/liter)						
		Fe	Cu	Zn	Cr	Ni	Pb	Al
2711	Test One, pH = 3.24	5.73	4.23	1.94	0.55	0.33	< D.L.	1.68
2712	Test Two, pH = 3.23	5.10	4.17	1.99	0.54	0.35	"	1.68
2713	Test Three, pH = 3.34	4.19	3.89	9.01	0.46	0.42	"	1.27

Notes: . Test performed according to EPA designated EP Toxicity test(27). EPA designated concentration of contaminants for characteristic toxicity (mg/l): 1.0 Cd, 5.0 Cr, 5.0 Pb.

Zinc solvent extraction in the Reister system using pH adjustment after two contacts works well. Interfaces are stable and controllable at 250 cc/min. (probably also to 450 cc/min.) Crud is not a problem. Gypsum forms in the strip cell but can be filtered and not returned to the extraction circuit (this is a bleed for Ca^{++} from the system). Iron is co-extracted with zinc. Zinc can be stripped by H_2SO_4, iron is not stripped. A bleed stream can be taken from the organic and treated with HCl to strip the iron. The resulting D_2EHPA can then be recycled to the zinc extraction circuit. Aluminum is co-extracted and provides a means to partially remove it from the system. A part of the aluminum is stripped into the H_2SO_4, a part into the HCl.

Chromium oxidation is a slow process. Better Cl_2 contact would accelerate this process. Electrooxidation may be an appropriate substitute. Slurry oxidation produces a small amount of solids, primarily $Cr(OH)_3$. This solid can be recycled to the initial leach system.

Chromium can be effectively stripped from the solution after oxidation by use of recycled $PbSO_4$. The solid formed is easily filtered or settled from solution. The lead chromate can be releached to produce a concentrated chromic acid solution. The rate of precipitation is rapid, therefore, a small reactor can be used.

Nickel can be stripped from the final solution by use of a Na_2S solution. The final sulfide treatment also helps to strip residual cations from solution.

The solution after nickel removal can almost entirely be recycled to the leach-jarosite steps as make-up water. The sulfide precipitation is rapid. Therefore, a small reactor can be used.

8.14. TEST ASSEMBLY EQUIPMENT

8.14.1. Unit Operation Equipment

A list of the equipment in the test assembly is presented in Table 8.131. The equipment list is organized according to the unit operations specified in flowsheet Figure 6.1.

8.14.2. Pictorial Presentation of Test Assembly Equipment

A series of photographs of the test assembly equipment is presented in Figures 8.27-31. Included are: the leach-jarosite system (Figure 8.27); filter press (Figure 8.28); small-scale SX testrack (Figure 8.29); Reister Solvent Extraction Testrack (Figure 8.30); and the chlorine oxidation and extraction system (Figure 8.31).

TABLE 8.131. TEST ASSEMBLY EQUIPMENT

Leach-Jarosite Precipitation

- Polypropylene vessel: 270 liter capacity; insulated with one-half inch fiberfax; contained within an epoxy coated steel liner vessel; mounted quartz immersion heaters, two 6,000 watt units, 240 volts; tight fitting acrylic top.

- One-half horsepower air driven NETTCO variable speed agitator; thirty-inch stainless steel impeller shaft, one-inch diameter; with a single eight-inch three blade impeller.

- Industrial Cole-Parmer pH controller and high temperature chemical resistant sensor model probe K-5660-00, K-5660-04.

- Associated solution pumps to supply reagents to vessel, such as sulfuric acid, hydrogen peroxide, potassium sulfate solution, potassium or sodium hydroxide.
- Two hundred liter polyethylene storage tank for decanting and storing solution for copper SX.

Solid-Liquid Separation

- An Ingersoll-Rand LASTA 360 ISD Press(46). The Lasta Filter Press is a horizontal filter press, and the 360 ISD model is the smallest in the Lasta Press line. There are six primary components of the 360 ISD Press: the frame, filter plate, diaphragm plate, moveable head, filter cloth, and hydraulic pump and cylinder.

1. Press Frame - The steel frame consists of front and rear fixed heads and two side rails bolted to them. It is the sructure which supports the plates, moveable head, and cylinder.

2. Filter Plate - The filter plate is a steel plate which rides on the side rails. It has a concave face which, when clamped against the diaphragm plate, forms half of the filtering chamber. The concave face is ribbed with vertical channels to provide a path for the filtrate to drain.

3. Diaphragm Plate - The diaphragm plate is a steel frame around two rubber diaphragms. When clamped against the filter plate, it forms the second half of the filtering chamber. The rubber surface is ribbed similarly to the filter plate to allow the filtrate to drain. When filled with water under pressure, the rubber expands, compressing the solids in the chamber.

4. Moveable Head - The moveable head is attached to the cylinder rod. It distributes the force of the hydraulic cylinder to create the clamping pressure on the plates.

5. Filter Cloth - The two panel filter cloth is a polypropylene weave which is hung between the filter and diaphragm plates. The slurry is pumped into the press, between the two panels. The weave of the cloth retains the solids and allows the filtrate to pass through to drain.

6. Hydraulic Pump and Cylinder - A double acting hydraulic cylinder is mounted in the rear fixed head. The cylinder rod extends and retracts to open, close, and clamp the plates. Oil to drive the cylinder is provided by a hand pump on top of the rear fixed head. The pump is equipped with a valve to direct the oil to the rod or head end of the cylinder.

Solvent Extraction

- Two Reister ten-cell solvent extraction testracks. Each cell has a one-gallon mixing chamber and a one-gallon settling chamber. Each mixing chamber is agitated with a one-seventh horsepower variable speed motor. Solution flow is conrolled by the agitator speed and its position over the solution inlet opening. Mixed solution continuously overflows a weir into the settling chamber. Organic phase separates to the top of the settling chamber and overflows a weir to an organic chamber. The aqueous phase and organic phase both flow continuously from the settling chamber.

- Associated solution pumps (flowrate adjusted to 500 cc/min.) to supply the aqueous feed, loaded organic, and strip solution feed to the SX chambers. Blue White C1760LP.

- Two hundred liter polyethylene storage vessel for collecting the raffinate from testrack; two required, one for raffinate from Cu SX and one for raffinate from zinc SX.

- pH controller (Cole-Parmer Model K-5660-00) for adjusting the aqueous phase pH from stage two of the four stage zinc SX set-up.

Copper Sulfate Crystallization

- Two liter reaction kettle with four-neck ground glass top and closed stirrer system. System will treat one-fourth to one-half of strip solution exiting the copper SX system. Anticipated treatment of ten percent bleed stream from strip solution; recycle of acid from copper sulfate crystallization cell to strip circuit.

- Solution pump (flow adjustable to 250 cc/min.), Blue-White Model C1760LP.

Copper Electrowinning

- Lambda LES-F regulated power supply, 0-9 v, 0-100 amp.

- Laboratory scale electrowinning cell, 13-inch by 6-inch by 8-inch chamber. Twenty-one electrode slots for 6.75-inch by 5.25-inch electrodes. Copper cathodes, lead anodes. System will treat strip solution at a current density of 20 amp/ft^2 at 2.5 volts. Copper content decreased by 5-10 gpl.

- Solution pump Blue-White Model C1760LP.

Zinc Sulfate Crystallization

- Two liter reaction kettle with four-neck ground glass top and closed stirrer system. System will treat up to one-sixth of strip solution exiting zinc solvent extraction system. Anticipated treatment of of ten percent bleed streams from strip solution; recycle of acid from zinc sulfate cyrstallization cell to strip circuit.
- Solution pump; Blue-White Model C1760LP (to 250 cc/min.).

Chromium Oxidation

Chlorine Oxidation

- Two hundred liter nalgene tank with vented top cover.

- One-fourth horsepower direct drive 115 v agitator with three-fourths inch diameter, 36-inch long epoxy coated shaft with four-inch impeller.

- Sparger for chlorine gas dispersion in solution slurry.

- pH monitor, Orion 601A.

- Solution pump for reagent addition, Blue-White Model C1760LP.

- Two 100 liter nalgene tanks.

- Two one-fourth horsepower direct drive 115 v agitators with three-fourths inch diameter, 36 inch long epoxy coated shaft with four-inch impeller.

- Chlorinator assembly.

- pH controller. Cole Parmer Model

- Chlorine tank.

Electrochemical Oxidation (This cell is not of sufficient size to treat a day's production of solution).

- Lambda LES-F regulated power supply, 0-9 v, 0-100 amp.

- Laboratory scale electrochemical cell, 13-inch by 6-inch by 8-inch. Two cation selective membrane dividers to separate anode chamber from cathode chamber. Lead anode, copper cathode. Volume and number of electrode chambers variable.

- Solution pump for anolyte recycle, Blue-White C1760LP.

- Plexaglas anode chamber with nafion membrane sides. Larger plexaglas cathode chamber.

- Circulation pumps, Masterflex double head, blue white catholyte recycle pump (C1760LP).

- Lambda LES-F regulated power supply, 0-9 v, 0-100 amps.

- Electrodes, solid lead sheet and lead wool sandwiched between two perforated lead sheets.

- Storage reservoirs, two, 30 liter nalgene tanks.

Chromium Precipitation

- One hundred liter polyethylene reactor vessel.

- One-half horsepower air driven direct drive agitator for variable speed control, 316 S.S. shaft, 36-inch length, 3/4-inch diameter shaft, 4.5-inch impeller.

- pH monitor, Orion 601A.

- Solution pumps for reagent addition and solution transfer.

Nickel Precipitation

- Two hundred liter nalgene tank.

- One-fourth horsepower, 110 v agitator, 316 S.S. One-inch diameter shaft, 36-inch long, two 8-inch diameter impellers.

- pH monitor, Orion 601A.

- Solution pump to provide reagent addition, Blue-White C1760LP.

- Solution pump for recycle to leach solution as make-up water, Cole-Parmer.

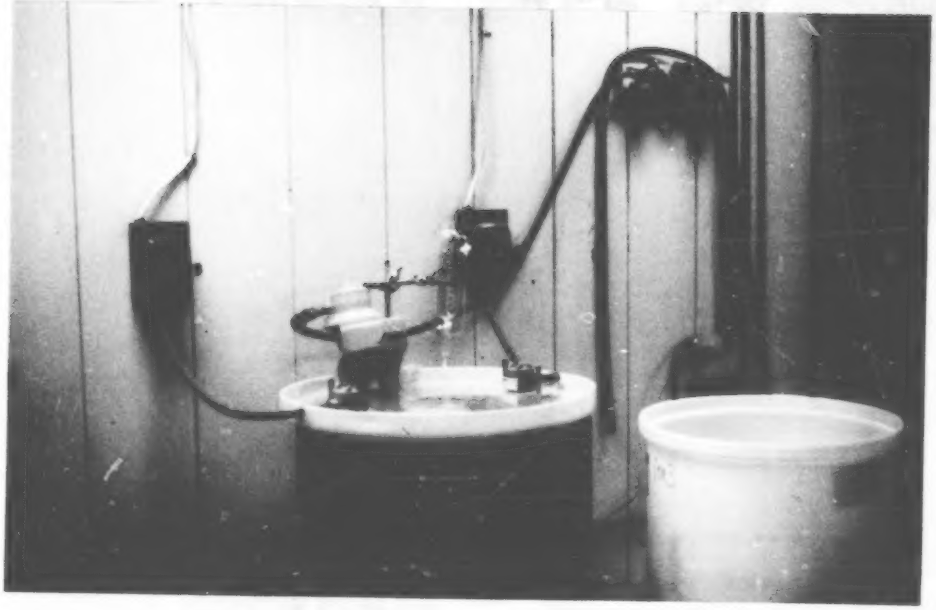

Figure 8.27. Leach-jarosite test system.

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best available copy.

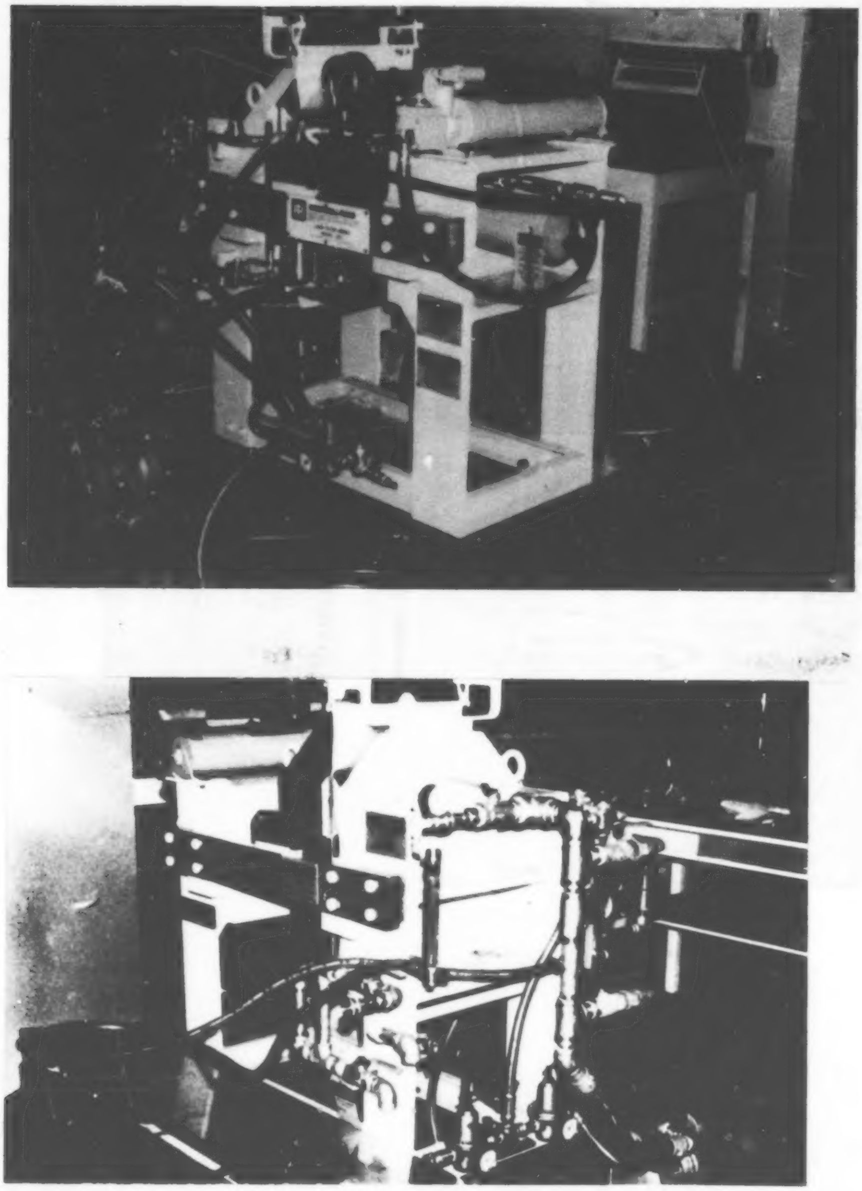

Figure 8.28. LASTA filter press.

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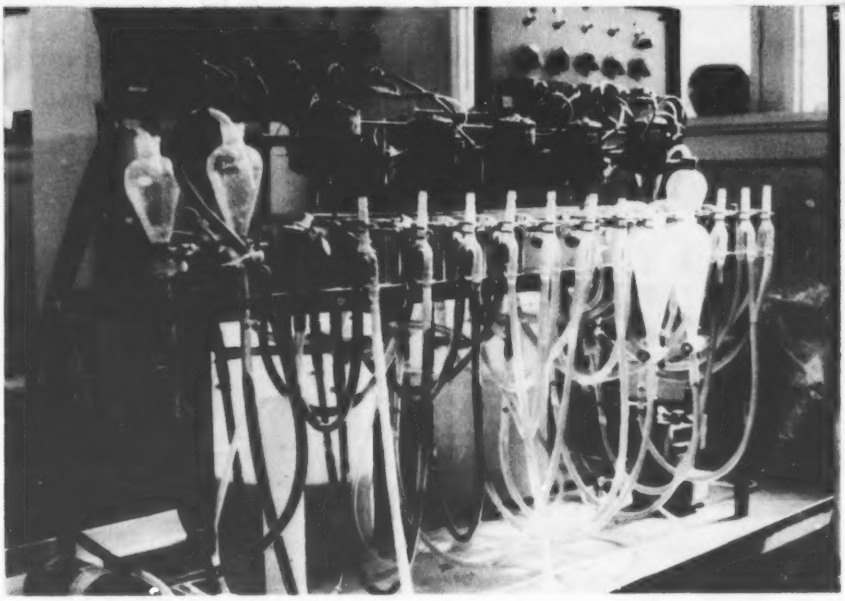
best available copy.



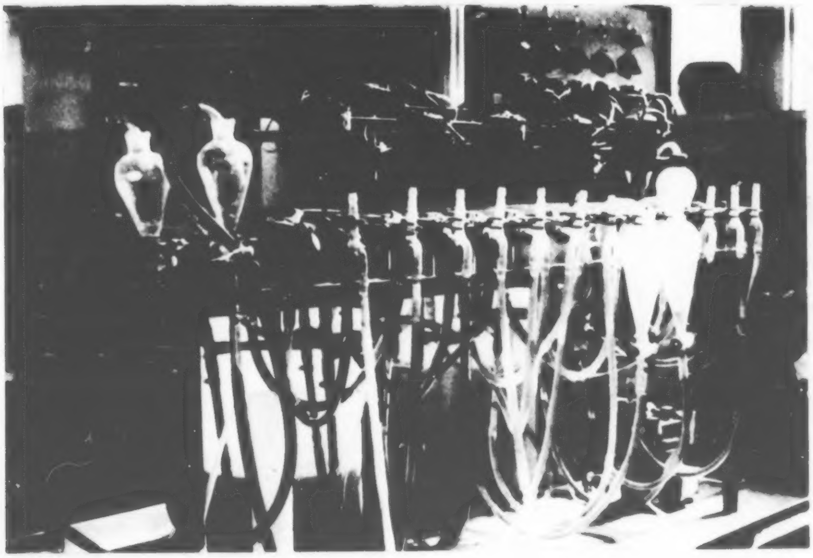


Figure 8.29. Small scale continuous solvent extraction system.
(Bell Engineering 600 cc system)

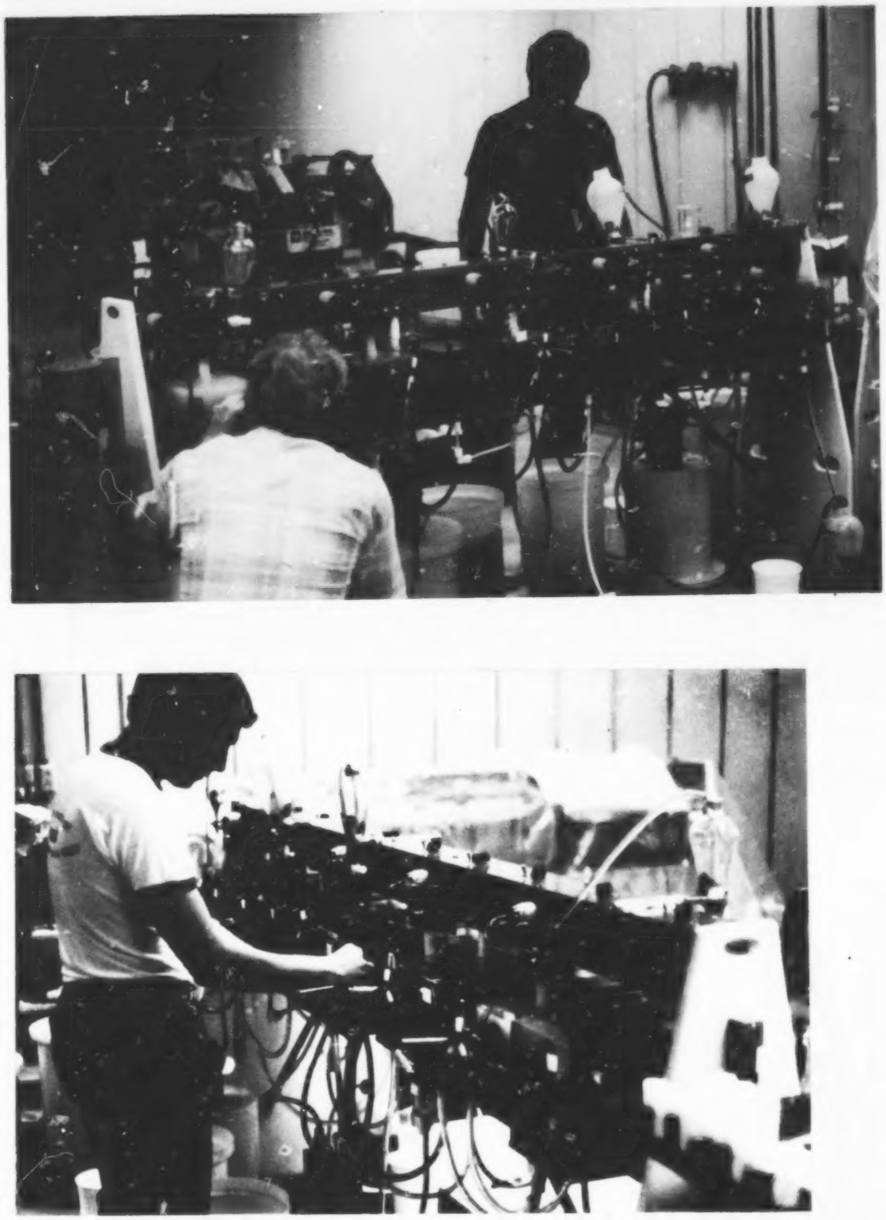


Figure 8.30. Reister one gallon mixer-settler continuous solvent extraction system.

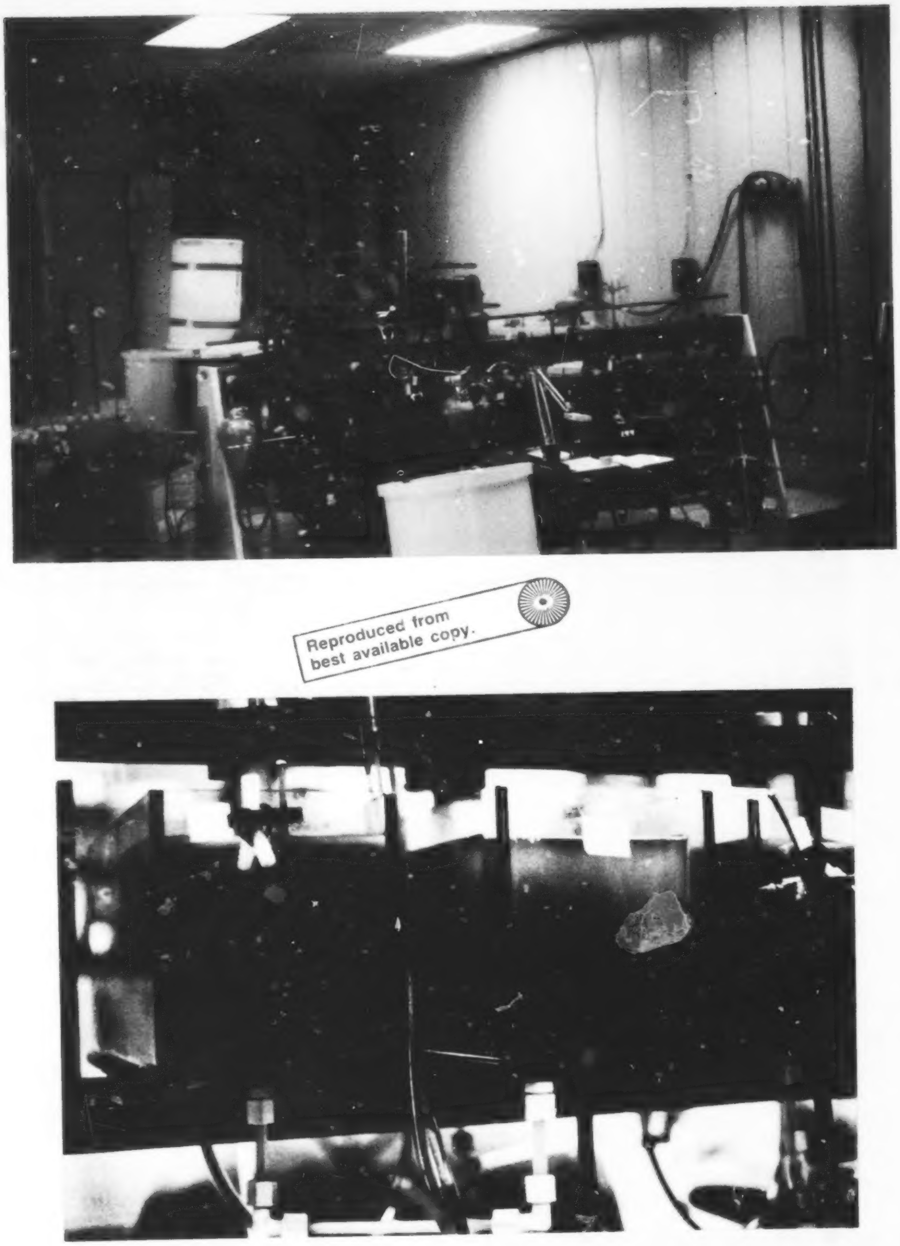


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Figure 8.30. Reister one gallon mixer-settler continuous solvent extraction system.

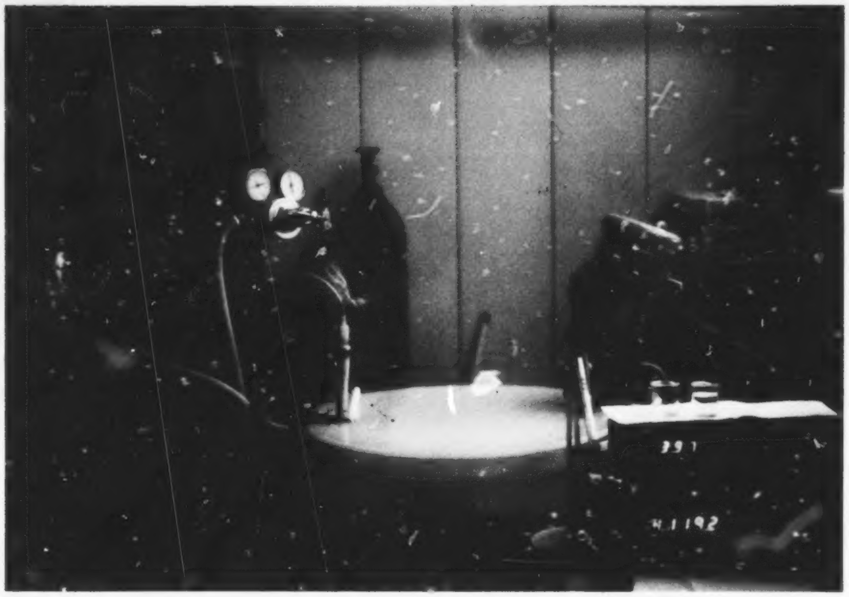

Figure 8.31. Chromium oxidation by chlorine sparging.

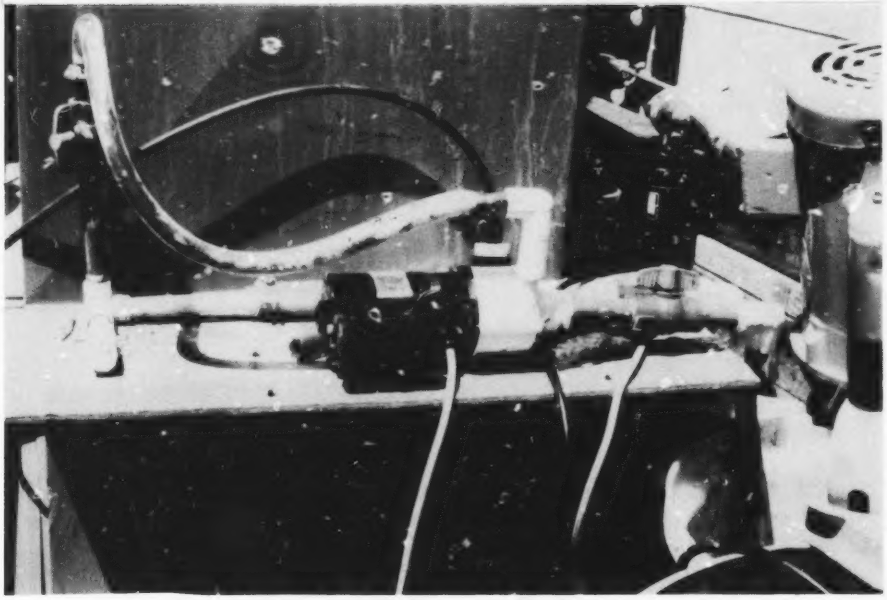

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Figure 8.32. Chromium oxidation by chlorinator system.

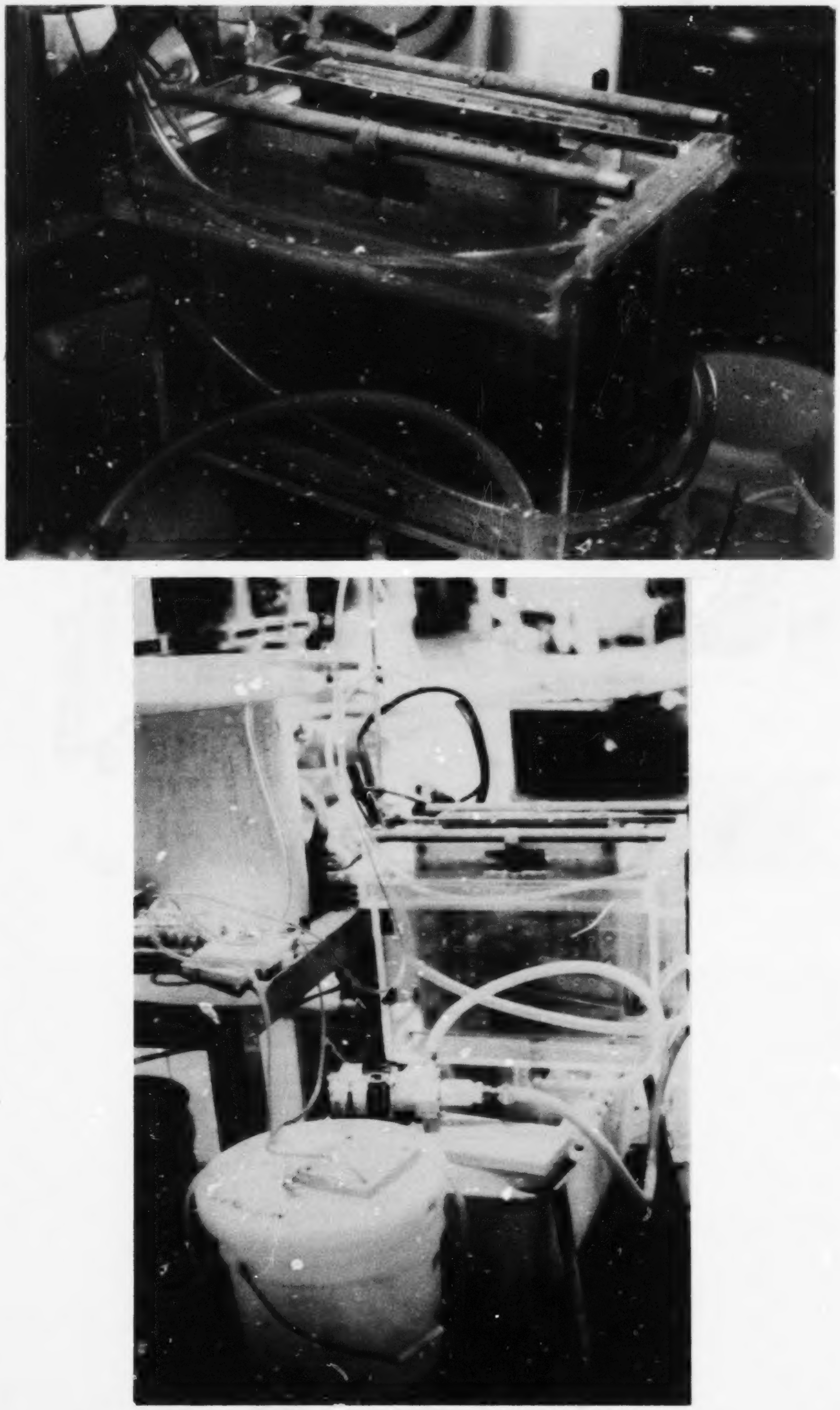

Figure 8.33. Electrochemical oxidation of chromium.

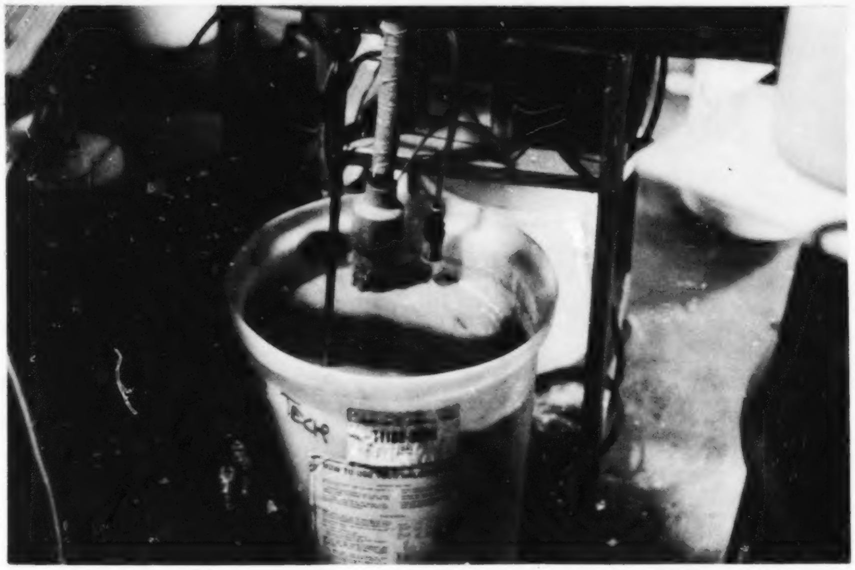

Figure 8.34. Lead chromate precipitation.

8.15. DETAILS OF ECONOMIC ANALYSIS

An economic analysis was presented in Section 6.4 for a 50 ton per day facility. The mass flows, equipment lists, factored capital cost data sheets, and operation cost estimates are presented in this section.

8.15.1. Leach-Jarosite Precipitation Filter

The equipment list is presented in Table 8.133 and the factored capital cost (FCC) is presented in Table 8.134. The operations cost is presented in Table 8.132. The total operation annual cost for this series of unit operations is \$343,000; 8.4 cents/lb. of jarosite plus leach residue.

8.15.2. Jarosite Ponding

The jarosite ponding cost is estimated from recent cost data on a state of the art mineral processing tailings pond. The result is presented in Table 8.135; the factored capital cost is \$390,500, the FCAC is \$108,200 and the operations cost is \$25,400. The total annual cost is \$133,600; the cost per pound is included with the cost for leaching and jarosite precipitation, i.e., 8.4 cents/lb.

8.15.3. Copper Solvent Extraction Electrowinning

Copper solvent extraction costs are estimated from data presented by Wood(50). The equipment (FCC and FCAC are presented in Table 8.136. The operation cost was presented previously in Table 8.131. The total annual cost for this series of unit operations is \$299,000; 80.2 cents/lb. of copper produced. This cost is approximately the same cost as the operating cost incurred by a current copper smelter (operating cost only, not including any capital cost). The estimated cost is greater than the current value of the copper product.

8.15.4. Zinc-Iron Solvent Extraction, Zinc Sulfate Crystallization

Zinc and iron solvent extraction are estimated from data presented by Wood(50). The equipment cost and factored capital cost are presented in Table

TABLE 8.132. OPERATING COST SUMMARY

Leach-Jarosite Precipitation-Filter

	COST($/Yr)
1. Reagents	
Acid: 1030 gal/d	11,000
KOH: 446 gal/d	47,200
Steam: available	
2. Labor	
$375/week (Oct. 9, 1984 Wall Street Journal average weekly pay) plus 30% benefits: $25350/man	
2 persons/shift; 3 shifts	152,100
3. Maintenance	
6% of Factored Capital Annual Cost (FCAC)	7,200
4. Power	
5% of FCAC	6,000
TOTAL	223,500

Jarosite Storage

1. Labor	
1 person, 1 shift	25,350

Copper Solvent Extraction

1. Reagents		
Lix 622: 150 gal	$6,840	
KERMAC 470B	920	
Acid, 330gal @ 180gpl H_2SO_4	15	
Total	7,775 (One time cost, included under capital cost)	
Organic loss: 13 mg/l		9,200
2. Labor		
2 persons/shift, 3 shifts		152,100

TABLE 8.132 CONTINUED

Chromium Oxidation, Precipitation, and Recovery

1. Reagents	
Acid: 60ppd H_2SO_4	600
NaOH: 0.7 tpd	69,300
$PbSO_4$: 2.52 tons (Start up only)	$4,300 (Included in capital)
2. Labor	
3 persons/shift; 3 shifts	228,200
3. Maintenance	
6% FCAC	30,200
4. Power	
5% FCAC	54,200
Electrooxidation, 3755 kwhr/tonne	25,200
TOTAL	407,700

Nickel Sulfide Recovery

1. Reagents	
Caustic: 29ppd	1,400
Phosphate: 7300 pounds (One time cost, 3200)	
Na_2S: 0.51 tpd	69,000
H_2SO_4: 35ppd	400
2. Labor	
2 persons/shift; 3 shifts	152,100
3.Maintenance	
5% FCAC	3,900
4. Power	
5% FCAC	3,200
TOTAL:	230,000

TABLE 8.132 CONTINUED

	COST ($/Yr)
3. Maintenance	
6% FCAC	5,200
4. Power	
5%FCAC	4,300
Electrowinning, 2500 kwhr/tonne Cu	35,100
TOTAL	205,900

Zinc and Iron Solvent Extraction

1. Reagents		
DEHPA: 790 gal	$16,850	
KERMAC 510: 1190 gal	1,300	
HCl: 700 pounds	450	
H_2SO_4: 1290 pounds	100	
Amberlite LA-2: 320 gal	8,000	
	26,700 (One time cost, included in capital cost)	
Organic loss: 13 mg/liter		4,100
Caustic: 0.057 t/d		5,600
2. Labor		
3 persons/shift; 3 shifts		228,200
3. Maintenance		
6% of FCAC		9,700
4. Power		
5% FCAC		8,100
25% FCAC for crystallizer power		14,000
TOTAL		269,700

TABLE 8.133. LEACH-JAROSITE PRECIPITATION-FILTER EQUIPMENT LIST

	COST($@M&S=500)
Feed System	
1. Vibratory feeder; $C = 965(20\ ft^2)^{0.559}$: 2 tph, 1 each.	5150
2. Recycle solution feeder; $C = 156(30gpm)^{0.38}$: rubber lined, 30 gpm, 1 each	570
3. Acid Cup feeder; $C = 1385(1cup)^{0.625}$: stainless steel, 0.7 gpm, 1 each.	1380
Leach System	
4. Leach tanks; $C = 27.5(1040gal)^{0.629}$: ss, 1040 gal, with agitator, 2 each.	4330
Jarosite Precipitation	
5. Precipitation tanks; $C = 27.5(4160)^{0.629}$: ss,4160 gal, with agitator, 3 each	15590
6. Thickener mechanism; $C = 1110(6.3\ ft)^{0.965}$ and Tank; $C = 7.13(1800)^{0.791}$: ss,1800 gal, 1 each.	9240
Filtering System	
7. Drum filter; $C = 8235(19\ ft^2)^{0.292}$: 19 ft^2 filtration area, 2 each.	38900
8. Repulp tank; $C= 27.5(100)^{0.629}$: ss, 100 gal, with agitator.	500
9. Storage tank; $C = 0.897(45{,}000\ gal)^{0.897}$: fiberglass, 45,000 gal, 1 each.	13400
TOTAL (M&S = 500)	89,100
TOTAL (M&S = 794)	141,500

TABLE 8.134. FACTORED CAPITAL COST FOR LEACH-JAROSITE PRECIPITATION-FILTER SYSTEM.

		Cost ($, M&S = 794)
1.	Purchased Equipment Costs	141,500
2.	Installed Equipment Costs (1.40 X Item 1)	198,100
3.	Process Piping (30% of 2)	59,400
4.	Instrumentation (10% of 2)	19,800
5.	Auxiliaries (5% of 2)	9,900
6.	Outside Lines (5% of 2)	9,900
7.	Total Physical Plant Costs (Sum of 2 through 6)	297,100
8.	Engineering and Construction (20% of 7)	59,400
9.	Contingencies (15% of 7)	44,600
10.	Size Factor (Small Commercial, 10% of 7)	29,700
11.	TOTAL PLANT FIXED CAPITAL COSTS	430,800

(1) Format from Mineral Processing Equipment Cost and Preliminary Capital Cost Estimations", E.A. Parkinson and A. L. Mular, Canadian Institute Mining and Metallurgy, V. 18, 1978.

YEARLY COST, Based on 60 Month Pay-Off Period, 12% Interest	$ 119,500
YEARLY OPERATING COST	$ 223,500
TOTAL YEARLY COST	$ 343,000

TABLE 8.135. JAROSITE PONDING EQUIPMENT LIST

The cost for jarosite ponding storage is estimated by determining the necessary pond capacity. Assumptions include: land is available, pond capacity great enough for ten year storage, controllable access only. The cost is estimated by ratioing the capacity of a known recent tailings pond as described by Jones (52); i.e., $\$6x10^6$(1980 cost) for a capacity of $7.3x10^6$ cubic meters; includes pumping, pH control, instrumentation, and monitoring.

The storage capacity needed for present estimate is 50,900 M^3.

$$\text{Cost} = 6x10^6 \left[50{,}900/7.3x10^6 \right]^{0.6} \left[794/620 \right]$$

$$= \$390{,}500.$$

This cost is estimated to be the current factored capital cost. The annualized cost is $108,200.

TABLE 8.136. COPPER SOLVENT EXTRACTION-ELECTROWINNING EQUIPMENT LIST AND FACTORED CAPITAL COST

The capital cost for the solvent extraction system is estimated from fabricated equipment cost for solvent extractors presented by Woods(50):

Data: Mixer-settlers

Size	Size Range	Cost($)	Exponent	M&S
1.5 lit/s	1.5-10 lit/s	7,000	0.4	600

(Includes: installed mixer-settler, including explosion proof motors, drives, and within module piping, concrete, steel, instruments, electrical, insulation and paint, and necessary labor.)

Factors for Materials

2.00 for 316 stainless steel
1.4 for rubber lined
2.0 for tankage and crud removal system

The capital cost for the present system is:

$$\text{Cost} = \$7{,}000\ [\text{lit/s,present/lit/s,Woods}]^{0.4}\ (\text{M\&S,now/M\&S,then})\text{x}\ (\text{No. of cells})(2.0\ \text{stainless steel})(2.0\ \text{for tankage})$$

$$\text{Cost} = \$7{,}000[1.86/1.5]^{0.4}\ (794/600)(2)(2)(5) = \$201{,}900$$

The capital cost for the electrowinning system is estimated from fabricated equipment cost presented by Woods (50):

Data:

Size	Size Range	Cost($)	Exponent	M&S
10^{10}g/y	2-60x10^9g/y	6x10^6	1.0	600

(Includes: cells, transformers, rectifiers, and electrical distribution)

The capital cost for the present system is:

$$\text{Cost} = [6\text{x}10^6][1.69\text{x}10^8/1\text{x}10^{10}]^{1.0}\ (794/600) = \$134{,}200$$

The total factored capital cost is, therefore,	$336,100
The FCAC is	93,100
The yearly operating cost is	205,900
The total yearly annualized cost is	$299,000

8.137. The total amount of operations cost for this series of unit operations is $453,000; 43.0 cents/lb. of zinc sulfate produced. This estimated cost is greater than the current value of the zinc sulfate product.

8.15.5. Chromium Oxidation, Precipitation and Chromic Acid Recovery

The equipment list is presented in Table 8.138 and the factored capital cost is presented in Table 8.139. The total annual operations cost for this series of unit operations is $911,300; 119.6 cents/lb. A potentially lower cost oxidation process is discussed in Section 6.4.

8.15.6. Nickel Recovery

The equipment list is presented in Table 8.140 and the factored capital cost is presented in Table 8.141. The total annual operations cost for this series of unit operations is $294,200; 49.9 cents/lb. Other alternate products were considered and discussed in Sections 6.4 and 8.15.7.

8.15.7. Alternates

8.15.7.1. SO_2-O_2 Chromium Oxidation, Nickel Oxide Production

The oxidation of chromium by chlorine or by electrochemical means is the most expensive unit operation in the sludge treatment flowsheet. If the cost of this unit operation could be decreased then the overall ROI would be increased. The substitution of an SO_2-O_2 oxidation system may prove to be a much cheaper means of oxidizing chromium. This substitution has been discussed in Section 6.4. The data for the substitution is presented in Tables 8.142, 8.143, and 8.144. The results on the overall ROI were presented previously in Tables 6.32a and 6.33a.

8.15.7.2. Copper Cementation

Copper cementation as a substitute for copper solvent extraction-electrowinning may be a more economical way to recover copper from a sludge leach solution stream. Biswas and Davenport report that (based on Ranchers' Exploration data) copper cementation by iron costs $0.35/kg copper less than

TABLE 8.137. ZINC-IRON SOLVENT EXTRACTION EQUIPMENT LIST AND FACTORED CAPITAL COST ESTIMATE

Cost data are not available for commercial zinc solvent extraction facilities. The equipment required is, however, similar to that required for copper solvent extraction. The major difference is the number of cells. For copper solvent extraction the previous cost was based on three stages of extraction, two stages of stripping. The zinc-iron solvent extraction is estimated based on the following assumptions:

a. Solvent extraction of iron and zinc requires ten cells for loading/stripping. The capital cost/cell (based on copper SX) is \$201,900/5 = \$40,400. Therefore, for iron and zinc the FCC = \$404,000.

b. Zinc sulfate crystallization is estimated: 990 gal per day of strip solution containing 140 gpl zinc. A batch crystallizer cost (57) is \$19,000 @ an M&S of 270. Therefore, the crystallizers present cost estimate is:

$$\text{Cost} = 19{,}000 \left[794/270 \right] = \$55{,}900,$$ the FCC is \$193,700(factors Table 6.29.)

c. The hydrochloric acid strip solution generated per day is 330 gal containing 18 gpl iron. A small pilot size SX plant to recover the HCl would be required using Amberlite LA-2 (34). The volume of solution to be treated is very small (330 gpd) compared to the volume of treated leach solution (42,000gpd).

Two mixer-settlers would be required for extraction and two for stripping. The cost for four cells is estimated from Wood to be:

$$\text{Cost} = 7000 \left[0.04 \text{ lit./sec.}/1.5 \text{ lit./sec.} \right]^{0} \left[794/600 \right]$$

= \$9,300/cell. This includes mixer-settlers, explosion proof motor, drive, piping, concrete, steel, instruments, electrical, insulation, paint. Total cost for four cells = \$37,200.

d. The concentrated ferric chloride may be a marketable product but neither a credit not a penality is taken for disposal.

The FCC total cost for solvent extraction, crystallization, and stripping of hydrochloric acid from the DEHPA strip solution is \$634,900. A one time cost for reagents is included in the capital cost, i.e., 26,700. Therefore, the total capital cost is \$661,600. The

The FCAC is	183,300
The operation cost (Table 8.137) is	269,700
The total annualized cost is	\$453,000

TABLE 8.138. CHROMIUM OXIDATION, PRECIPITATION, AND RECOVERY SYSTEM EQUIPMENT LIST

		COST($@M&S=500)
1.	Storage tank; $C = 0.897(45{,}000\text{gal})^{0.897}$: Fiberglass, 2 each.	26,800
2.	Electrochemical oxidation cells 3000 gal, 1500 amps, 15 units	480,000 Current
3.	Precipitation vessels; $C = 27.5(1040)^{0.629}$: Stainless steel, 1040 gal, with agitator, 2 each.	4,350
4.	Filter drum; $C = 8235(19)^{0.292}$: 19 ft^2 filtration area, 2 each.	38,900
5.	Releach vessel ss, 100 gal, with agitator, 1 each	1,000
	TOTAL (excluding 2)	71,000
	TOTAL (M&S =794)	112,800
	TOTAL (including 2)	592,800
	TOTAL (including one time cost of lead sulfate)	597,100

TABLE 8.139. FACTORED CAPITAL COST FOR CHROMIUM OXIDATION, PRECIPITATION AND RECOVERY

		Cost ($, M&S = 794)
1.	Purchased Equipment Costs	597,100
2.	Installed Equipment Costs (1.40 X Item 1)	835,900
3.	Process Piping (30% of 2)	250,800
4.	Instrumentation (10% of 2)	83,600
5.	Auxiliaries (5% of 2)	41,800
6.	Outside Lines (5% of 2)	41,800
7.	Total Physical Plant Costs (Sum of 2 through 6)	1,253,900
8.	Engineering and Construction (20% of 7)	250,800
9.	Contingencies (15% of 7)	188,100
10.	Size Factor (Small Commercial, 10% of 7)	125,400
11.	TOTAL PLANT FIXED CAPITAL COSTS	1,818,200

(1) Format from Mineral Processing Equipment Cost and Preliminary Capital Cost Estimations", E. A. Parkinson and A. L. Mular, Canadian Institute Mining and Metallurgy, V. 18, 1978.

YEARLY COST, Based on 60 Month Pay-Off Period, 12% Interest	$ 503,600
YEARLY OPERATING COST	$ 407,700
TOTAL YEARLY COST	$ 911,300

TABLE 8.140. NICKEL SULFIDE PRECIPITATION SYSTEM EQUIPMENT LIST

	COST($@M&S=500)
1. Precipitation vessels; $C = 27.5(1040)^{0.629}$: Stainless steel, 1040 gal, with agitator, 2 each.	4,400
2. Filter drum; $C = 8235(19)^{0.292}$: 19 ft^2 filtration area, 2 each	38,900
3. Releach vessel; ss, 100 gal, with agitator, 1 each	500
4. Precipitation vessel; $C = 30.0(100)^{0.58}$: Rubber lined stainless steel, 100 gal, with agitator, pressure vessel, 1 each	500
TOTAL	45,900
TOTAL (M&S = 794)	72,900
TOTAL (including one time cost for phosphate)	76,100

TABLE 8.141. FACTORED CAPITAL COST FOR NICKEL RECOVERY

		Cost ($, M&S = 794)
1.	Purchased Equipment Costs	76,100
2.	Installed Equipment Costs (1.40 X Item 1)	106,500
3.	Process Piping (30% of 2)	32,000
4.	Instrumentation (10% of 2)	10,600
5.	Auxiliaries (5% of 2)	5,300
6.	Outside Lines (5% of 2)	5,300
7.	Total Physical Plant Costs (Sum of 2 through 6)	159,700
8.	Engineering and Construction (20% of 7)	31,900
9.	Contingencies (15% of 7)	24,000
10.	Size Factor (Small Commercial, 10% of 7)	16,000
11.	TOTAL PLANT FIXED CAPITAL COSTS (Sum of 7 through 10)	231,600

(1) Format from "Mineral Processing Equipment Cost and Preliminary Capital Cost Estimations", E. A. Parkinson and A. L. Mular, Canadian Institute Mining and Metallurgy, V. 18, 1978.

YEARLY COST, Based on 60 Month Pay-Off Period, 12% Interest	$ 64,200
YEARLY OPERATING COST	$ 230,000
TOTAL YEARLY COST	$ 294,200

TABLE 8.142. INCO SO_2-O_2 OXIDATION EQUIPMENT LIST

	COST($@M&S=500)
1. Oxidation cells; $C = 472(400)^{0.52}$: Flotation agitation cells, covered and vented, 400 ft^3, 3 each	50,700
2. Drum Filter; $C = 8235(19)^{0.292}$: 19 ft^2 filtration area, 1 each	19,500
3. Rotary kiln Includes refractory lining capable of 1200°C, firing system, hot cyclone, water cooling, 6' diam., 8' length, 30 tpd capacity (only need a 1 tpd capacity), $140,000 @ M&S 545, Fully instrumented.	128,400
4. Covered high temperature discharge conveyor 18"x25', $8,000 @ M&S 300	13,300
5. Bag collector Small gas flows, cost includes motor and drive, $2,500 @ M&S 300	4,000
TOTAL	215,900
TOTAL (M&S = 794)	342,800

TABLE 8.143. FACTORED CAPITAL COST FOR SO_2-O_2 CHROMIUM OXIDATION, NiO PRODUCTION SYSTEM

		Cost ($, M&S = 794
1.	Purchased Equipment Costs	342,800
2.	Installed Equipment Costs (1.40 X Item 1)	479,900
3.	Process Piping (30% of 2)	144,000
4.	Instrumentation (10% of 2)	48,000
5.	Auxiliaries (5% of 2)	24,000
6.	Outside Lines (5% of 2)	24,000
7.	Total Physical Plant Costs (Sum of 2 through 6)	719,900
8.	Engineering and Construction (20% of 7)	144,000
9.	Contingencies (15% of 7)	108,000
10.	Size Factor (Small Commercial, 10% of 7)	72,000
11.	TOTAL PLANT FIXED CAPITAL COSTS (Sum of 7 through 10)	1,043,900

(1) Format from "Mineral Processing Equipment Cost and Preliminary Capital Cost Estimations", E. A. Parkinson and A. L. Mular, Canadian Institute Mining and Metallurgy, V. 18, 1978.

YEARLY COST, Based on 60 Month Pay-Off Period, 12% Interest	$ 289,200
YEARLY OPERATING COST	$ 484,600
TOTAL YEARLY COST	$ 773,800

TABLE 8.144. SO_2 - O_2 OPERATING COST SUMMARY

	COST($/Yr)
1. Reagents	
Caustic: 47.0 tpd	14,100
Liquid SO_2:	103,400
2. Labor	
2 persons/shift; 3 shifts	152,100
3. Maintenance	
5% FCAC	17,400
4. Energy	
5% FCAC	14,500
Fuel for kiln, \$6/1000 ft^3	31,800
Electrical for kiln motors, 160 HP, 2 each, 0.08 $/kwh	151,300
TOTAL	484,600

solvent extraction-electrowinning. This comparison was made in 1975. If the assumption is made that the cost difference then is the same as the cost difference now, then the cost for producing 1130 pounds per day of cement copper would be $180/day less than for producing electrowon copper by SX-EW. This cost includes capital cost and operating cost. Therefore, the total annual cost, presented in Table 6.30, of $299,000 should be reduced by $59,400; the new total amount would be $239,600. However, the value of the cement copper would be approximately one-half the value of electrowon copper. The value of the electrowon copper was estimated to be $223,700. Therefore, the value of cement copper would be $111,900. The difference between what is saved in annual cost and the loss of value for the new product would, in fact, make the ROI less rather than greater.

8.15.7.3. Production of $CuSO_4$

An alternative to be explored is the relative cost of recovering crystallized copper sulfate monohydrate instead of copper metal. If one assumes that the electrowinning unit operation has approximately the same annualized cost as the crystallization unit operation then the difference in return would be the difference in the value of 1130 pounds per day copper ($0.60/lb.) and 3480 pounds per day of copper sulfate monohydrate ($0.75/lb.). The yearly value difference is $637,600. This would change the ROI from 41 to 51 percent compared to the electrochemical oxidation flowsheet; and would change the ROI from 69 to 83 percent compared to the SO_2-O_2 oxidation flowsheet. The cost differences are interesting enough so that the alternate should be further considered.

8.15.7.4. Solvent Extraction of Nickel, Electrowinning of Nickel, Precipitation of Chromiun Hydroxide, Production of Chromium Oxide

An attractive alternate is a major modification to the original flowsheet that depends on the ability to selectively extract nickel from the leach without removal of chromium. This appears to be possible by use of the D_2EHPA-EHO or LIX63-D_2EHPA solvent extraction reagents. Further research is needed to verify the conditions needed for such a system. Also, one should be aware that such a unit operation is more risky than previously suggested alternatives because SX of nickel by these reagents is not presently commercially produced.

The alternate flowsheet was presented previously in Figure 6.7b. The equipment list and factored capital cost estimates are presented in Table 8.145; operating cost is presented in Table 8.146.

8.15.8. Computer Mass Balances for 50 TPD Economic Analysis

The computer mass balance data for the 50 TPD economic analysis is presented in Table 8.147. The computer mass balance program and software are presented in a separate manual.

TABLE 8.145. SOLVENT EXTRACTION OF NICKEL, ELECTROWINNING OF NICKEL, PRECIPITATION OF CHROMIUM HYDROXIDE, AND PRODUCTION OF CHROMIUM OXIDE

Solvent Extraction and Electrowinning of Nickel

The FCC determined previously per mixer-settler cell for the flow capacity of the present system was $40,400. The present system requires five cells; $201,900.

The electrowinning system FCC is:

$$\text{Cost} = 6\text{x}10^6 \left[1.72\text{x}10^8 \text{gpy Ni}/1\text{x}10^{10}\right]^{1.0} (794/600)$$

$$= \$136,600$$

The FCC for SX and EW is: $338,500 (M&S 794)

The FCAC is: 93,800

Precipitation of Chromium Hydroxide and Production of Chromium Oxide

Equipment List	COST($@M&S 500)
1. Precipitation vessels: $C = 27.5(1040)^{0.629}$: stainless steel, 1040 gal, with agitator, 2 each	4,400
2. Filter drum; $C = 8235(19)^{0.292}$: 19 ft^2 area, 1 each	19,500
3. Rotary kiln; Includes refractory lining capable of 1200°C, firing system, hot cyclone, water cooling, 6' diam., 8' length, 30 tpd capacity (only need 1tpd capacity), $140,000 @ M&S 545, fully instrumented	128,400
4. Covered High temperature discharge conveyor; 18"x25', $8,000 @ M&S 300	13,300
5. Bag Collector; Small gas flow, cost includes motor and drive, $2,500 @ M&S 300	4,000
Total Equipment Cost (M&S 500)	169,600
Total (M&S 794)	269,300
FCC	819,800
FCAC	227,100
TOTAL FCC for SX, EW, Cr_2O_3 Production:	1,158,300
TOTAL FCAC for SX, EW, Cr_2O_3 Production:	320,800

TABLE 8.146. OPERATING COST FOR TABLE 8.145 SEQUENCE

		COST($/Y)
1. Reagents		
LIX 63 (12.5%): 125 gal	$6,200	
DEHPA (16.0%): 160 gal	3,400	
KERMAC 510: 715 gal	800	
	10,400 (one time cost, included in capital cost)	
Organic loss: 13 mg/liter		6,900
Caustic: 74 tpy		22,200
2. Labor		
2 persons/shift; 3 shifts		152,100
3. Maintenance		
5% FCAC		19,200
4. Energy		
5% FCAC		16,000
Fuel for kiln, $6/1000ft^3$		31,800
Electrical for kiln motors, 160 HP, 2 each, 0.08$/kwh		151,300
Electrowinning; 3755 kwh/tonne Ni, 173 tpy		52,000
TOTAL OPERATION COST		$451,500

TABLE 8.147. COMPUTER MASS BALANCE DATA FOR 50 TPD SLUDGE TREATMENT FLOWSHEET

```
                 ****************************************
                         COMPOSITE SLUDGE PROGRAM
                 ****************************************


HERE IS THE COMPOSITION OF THE COMPOSITE SLUDGE (W/O)
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
  5.00   5.00   0.00   5.00   5.00   1.00   1.00   7.50   2.00   0.00  20.00   2.00

THE % SOLIDS IN COMP. SLUDGE : 25.00

THE COMPOSITION OF THE COMPOSITE SLUDGE
    GIVEN AS W/O METAL HYDROXIDES
    CA AND PB ARE GIVEN AS SULFATES
    SI AND P ARE GIVEN AS OXIDES
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
  7.68   7.90   0.00   7.60   8.27   3.40   1.74  12.07   5.78   0.00  42.78   6.13

THE TOTAL W/O OF THE HYDROXIDES, OXIDES AND SULFATES ----
                    ***** 103.34  *****


                  ****************************************
                               LEACH MODULE
                                  ENTRY
                  ****************************************


//////////////////////////////
STARTING CONDITIONS....(SLUDGE EXCLUDING RECYCLES)

COMPOSITION (W/O METALS) .....
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
  5.00   5.00   0.00   5.00   5.00   1.00   1.00   7.50   2.00   0.00  20.00   2.00

COMPOSITION (W/O METAL HYDROXIDES, EXCEPT CA AND PB SULFATES ....
         AND SI AND P OXIDES
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
  7.68   7.90   0.00   7.60   8.27   3.40   1.74  12.07   5.78   0.00  42.78   6.13
```

TABLE 8.147. CONTINUED

```
EXTRACTIONS - % - ......
   CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
 93.70 95.90 100.00 95.10 96.50 15.00 100.00 92.00 96.90  0.00   0.00 100.00

% SOLIDS IN SLUDGE, DENSITY (G/CM3) OF SLUDGE
        25.00                 3.50

THE AMOUNT OF SLUDGE TREATED: (PPD) ... 100000.

% EXCESS CAPACITY IN THE VESSEL, RESIDENCE TIME IN THE VESSEL (HRS.) ...
                 20.00          0.50

//////////////////////////////
RESULTS.........(INCLUDING RECYCLE SOLIDS/SOLNS)

THE ACTUAL AMOUNT OF SOLIDS TREATED: (PPD) 25000.0

THE ACTUAL AMOUNT OF METALS IN THE SOLID: (PPD)
   CU      NI      CD     ZN      CR      CA     NA     FE      AL     PB     SI     P
 1250.00 1250.00  0.00 1250.00 1250.00 250.00 250.00 1875.00 500.00  0.00 5000.0

THE ACTUAL AMOUNT OF METALS EXTRACTED: (PPD)
   CU      NI      CD     ZN      CR      CA     NA     FE      AL     PB     SI     P
 1171.25 1198.75  0.00 1188.75 1206.25 37.50 250.00 1725.00 484.50  0.00  0.00 0

ACID AVAILABLE FROM RECYCLES: (PPD)  0.00

AMT. X STOIC. OF ACID FOR CALC.: 1.0


THE AMOUNT OF ACID CONSUMED:......
     PPD       LIT/DAY
  15858.7    3890.10

THE CONC. OF THE ADDED ACID: (GPL)  60.00

////////////////////////////////
IN THE VESSEL .......

THE AMOUNT OF LIQUID IN THE LEACH VESSEL: (LIT/DAY) 153927.
THE AMOUNT OF SOLIDS IN THE LEACH VESSEL: (LIT/DAY) 3241.43
THE TOTAL VOLUME: (LIT/DAY) 157168.
THE W/O SOLIDS IN THE LEACH VESSEL:  5.79

THE TOTAL VESSEL VOL. WITH 20.00% EXCESS CAPACITY: (LIT/DAY) 188602.

THE SIZE OF THE LEACH VESSEL WITH  0.5 HOURS
          RESIDENCE TIME IS: (LITERS) 3929.21
```

TABLE 8.147. CONTINUED

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////////////////////////////////////
AFTER THE LEACH ......

THE AMOUNT OF RESIDUE: (PPD) 11236.7
THE ACTUAL AMOUNT OF METALS IN THE RESIDUE: (PPD)
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
 78.75 51.25  0.00 61.25 43.75 212.50  0.00 150.00 15.50  0.00 5000.00  0.00

THE W/O METALS IN THIS RESIDUE ....
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.70   0.46   0.00   0.55   0.39   1.89   0.00   1.33   0.14   0.00  44.50   0.00

THE % SOLIDS COMING FROM THE LEACH VESSEL: 2.69

THE SOLUTION COMP: (GPL)
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  3.45   3.53   0.00   3.50   3.55   0.11   0.74   5.08   1.43   0.00   0.00   1.47

THE TOTAL GPL IN THE LEACH SOLN: 22.87
THE AMOUNT OF EXCESS ACID IN THE LEACH SOLUTION: (GPL)  0.00


****************************************************************
                      SOLID/LIQUID SEPARATION
****************************************************************

/////////////////////
STARTING CONDITIONS .....

AMOUNT OF SOLIDS ENTERING S/L SEPARATION: (PPD) 11236.7
AMOUNT OF LIQUID ENTERING S/L SEPARATION: (LIT/DAY) 153927.
% SOLIDS IN FIRST FILTER CAKE (NOT FROM REPULPS):  70.00

# REPULP ---    1
%SOLIDS   REPULP X  GPL ACID
 70.00      5.00     60.00

////////////////////////

THE RESULTS ......

THE AMOUNT OF SOLUTION EXITING FIRST S/L SEPARATION (LIT/DAY)  151943.

ITS COMPOSITION (GPL) .....
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  3.45   3.53   0.00   3.50   3.55   0.11   0.74   5.08   1.43   0.00   0.00   1.47

THE AMOUNT OF SOLUTION TRAPPED IN THE FILTER CAKE: (LIT/DAY) 1983.71

THE POTENTIAL LOSS OF METAL VALUES IN THE TRAPPED SOLN. (PPD)
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
 15.094 15.449 0.000 15.320 15.545 0.483 3.222 22.231 6.244 0.000 0.000 6.444
```

TABLE 8.147. CONTINUED

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/////////////////////////////////////
THE AMOUNT OF SOLUTION EXITING REPULP   1 IS : (LIT/DAY)  9824.10

ITS COMPOSITION (GPL) ....
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.58   0.59   0.00   0.58   0.59   0.02   0.12   0.85   0.24   0.00   0.00   0.25

THE PPD OF EACH METAL IN THE EXITING SOLUTION
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
 12.459 12.751 0.000 12.645 12.831 0.399 2.659 18.349 5.154 0.000 0.000 5.319

THE AMOUNT OF SOLUTION TRAPPED IN THE FILTER CAKE: (LIT/DAY) 2078.18

THE POTENTIAL LOSS OF METALS IN THE TRAPPED SOLN: (PPD)
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
 2.636 2.697 0.000 2.675 2.714 0.084 0.563 3.882 1.090 0.000 0.000 1.125

/////////////////////////////////////

THE AMOUNT OF SOLUTION EXITING SLSEP AFTER ALL REPULPS (LIT/DAY)  161767.

ITS COMPOSITION (GPL) ....
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  3.28   3.35   0.00   3.33   3.37   0.10   0.70   4.83   1.36   0.00   0.00   1.40

THE PPD METAL LOST IN THE FINAL FILTER CAKE :
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
 2.636 2.697 0.000 2.675 2.714 0.084 0.563 3.882 1.090 0.000 0.000 1.125


THE COMPOSITION OF THE FINAL FILTER CAKE ........
PPD OF SOLID ... 11236.7
PPD OF SOLUTION .... 4815.74
LIT/DAY OF TRAPPED SOLN: 2078.18

THE AMOUNT OF ACID EXITING IN THE FINAL SOLUTION
   (IN GPL)            3.68

THE PPD OF METALS EXITING FROM REPULPS:
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
 12.46 12.75  0.00 12.64 12.83   0.40   2.66  18.35   5.15   0.00   0.00   5.32
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TABLE 8.147. CONTINUED

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**************************************

     GENERAL EXTRACTION PROGRAM :  JAROSITE PRECIPITAION

**************************************


GPL IN STARTING SOLUTION:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI       P
  3.28    3.35    0.00    3.33    3.37    0.10    0.70    4.83    1.36    0.00    0.00    1.40

THE LITERS/DAY STARTING SOLUTION:  161767.

THE PERCENT EXTRACTIONS:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI       P
   2.7     3.6     6.2     2.0    15.0     0.0     0.0    97.0    44.5   100.0   100.0    50.0


 POUNDS METALS ENTERING PROCESS:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI       P
 1168.6  1196.1    0.0  1186.1  1203.5   37.4  249.4  1721.1  483.4    0.0     0.0 498.9

NEW GPL VALUES - SOLUTION EXITING PROCESS :
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI       P
  3.19    3.23    0.00    3.26    2.87    0.10    0.70    0.14    0.75    0.00    0.00    0.70


THE MOLE. WT. OF THE PRECIP. SPECIES:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI       P
  97.5    92.7   146.4    99.4   103.0   130.0     0.0   501.0    78.0   248.0    64.0    65.0

THE MOLES OF PRECIP. SPECIES PRODUCED PER MOLE METAL:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI       P
   1.0     1.0     1.0     1.0     1.0     1.0     1.0     0.3     1.0     1.0     1.0     1.0

THE PPD OF EACH PRECIP. SPECIES:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI       P
  48.4    68.0     0.0    36.1   357.5     0.0     0.0  4492.8   621.9     0.0     0.0   523.4

THE TOTAL PPD OF SOLID SPECIES PRECIP:  6148.1

GPL ACID IN SOLN:  0.0


****************************************************************
                    SOLID/LIQUID SEPARATION
****************************************************************

////////////////////
STARTING CONDITIONS .....
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TABLE 8.147. CONTINUED

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AMOUNT OF SOLIDS ENTERING S/L SEPARATION: (PPD) 6148.06
AMOUNT OF LIQUID ENTERING S/L SEPARATION: (LIT/DAY) 161767.
% SOLIDS IN FIRST FILTER CAKE (NOT FROM REPULPS):  70.00

* REPULP ---     1
%SOLIDS    REPULP X  GPL ACID
 70.00       1.00     60.00


///////////////////////

THE RESULTS ......

THE AMOUNT OF SOLUTION EXITING FIRST S/L SEPARATION (LIT/DAY)  160682.

ITS COMPOSITION (GPL) .....
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
  3.19   3.23   0.00   3.26   2.87   0.10   0.70   0.14   0.75   0.00   0.00   0.70

THE AMOUNT OF SOLUTION TRAPPED IN THE FILTER CAKE: (LIT/DAY) 1085.37

THE POTENTIAL LOSS OF METAL VALUES IN THE TRAPPED SOLN. (PPD)
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
 7.629  7.736  0.000  7.799  6.864  0.251  1.674  0.346  1.800  0.000  0.000  1.674

//////////'//////////////////////////
THE AMOUNT OF SOLUTION EXITING REPULP   1 IS : (LIT/DAY)  1033.69

ITS COMPOSITION (GPL) ....
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
  1.59   1.62   0.00   1.63   1.43   0.05   0.35   0.07   0.38   0.00   0.00   0.35

THE PPD OF EACH METAL IN THE EXITING SOLUTION
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
 3.633  3.684  0.000  3.714  3.268  0.120  0.797  0.165  0.857  0.000  0.000  0.797

THE AMOUNT OF SOLUTION TRAPPED IN THE FILTER CAKE: (LIT/DAY) 1137.05

THE POTENTIAL LOSS OF METALS IN THE TRAPPED SOLN: (PPD)
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
 3.996  4.052  0.000  4.085  3.595  0.131  0.877  0.181  0.943  0.000  0.000  0.877
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TABLE 8.147. CONTINUED

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THE AMOUNT OF SOLUTION EXITING SLSEP AFTER ALL REPULPS (LIT/DAY)  161716.

ITS COMPOSITION (GPL) ....
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
  3.18   3.22   0.00   3.25   2.86   0.10   0.70   0.14   0.75   0.00   0.00   0.70

THE PPD METAL LOST IN THE FINAL FILTER CAKE :
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
 3.996  4.052  0.000  4.085  3.595  0.131  0.877  0.181  0.943  0.000  0.000  0.877

THE COMPOSITION OF THE FINAL FILTER CAKE ........
PPD OF SOLID ... 6148.06
PPD OF SOLUTION .... 2634.88
LIT/DAY OF TRAPPED SOLN: 1137.05

THE AMOUNT OF ACID EXITING IN THE FINAL SOLUTION
   (IN GPL)             0.40

THE PPD OF METALS EXITING FROM REPULPS:
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
  3.63   3.68   0.00   3.71   3.27   0.12   0.80   0.16   0.86   0.00   0.00   0.80

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 THE SOLVENT EXTRACTION CONDITIONS ARE AS FOLLOWS:

      TEMPERATURE (IN DEGREES CENTIGRADE):  50
      CONTACT TIME (IN MINUTES): 3.0
      O/A RATIO:  1.00

 THE VOLUME FLOW RATE(L/D) OF ORGANIC SOLUTION REQUIRED IS:  161716.
      THE VOLUME % LIX 622 IN THE ORGANIC SOLUTION IS:  15.00
      THE VOLUME % KERMAC 510 IN THE ORGANIC SOLUTION IS:  85.00
      THE VOLUME % 0 IN THE ORGANIC SOLUTION IS:  0.00
       198.0 SETS OF MIXING TANKS ARE REQUIRED, 3 STAGES PER SET.
****************************************************************

THE  PH FOR STAGE  1 IS  1.75

THE EXTRACTION EFFICIENCYS FOR STAGE  1 ARE:
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
 92.10   0.00   0.00   0.00   0.00   0.00   0.00   1.00   0.00   0.00   0.00  28.00
****************************************************************

THE AQUEOUS EXITING STAGE  1 CONTAINS (G/L):
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI      P
  0.25   3.22   0.00   3.25   2.86   0.10   0.70   0.14   0.75   0.00   0.00   0.50
****************************************************************
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TABLE 8.147. CONTINUED

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***************************************************************

THE  PH FOR STAGE  2 IS  1.50

THE EXTRACTION EFFICIENCYS FOR STAGE  2 ARE:
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
 85.20  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00
***************************************************************

THE AQUEOUS EXITING STAGE  2 CONTAINS (G/L):
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.04  3.22  0.00  3.25  2.86  0.10  0.70  0.14  0.75  0.00  0.00  0.50
***************************************************************

THE ORGANIC EXITING STAGE  2 CONTAINS (G/L):
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.23  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00
******************************************************

***************************************************************

THE  PH FOR STAGE  3 IS  1.30

THE EXTRACTION EFFICIENCYS FOR STAGE  3 ARE:
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
 43.80  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00
***************************************************************

THE AQUEOUS EXITING STAGE  3 CONTAINS (G/L):
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.02  3.22  0.00  3.25  2.86  0.10  0.70  0.14  0.75  0.00  0.00  0.50
***************************************************************

THE ORGANIC EXITING STAGE  3 CONTAINS (G/L):
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.02  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00
******************************************************
***************************************************************

THE ORGANIC TO THE STRIPPING PROCESS CONTAINS:
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  3.16  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00  0.20


THE FINAL AQUEOUS SOLUTION CONTAINS:
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.02  3.22  0.00  3.25  2.86  0.10  0.70  0.14  0.75  0.00  0.00  0.50
***************************************************************
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TABLE 8.147. CONTINUED

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*****************************************************************

                      SX ZINC AND IRON

*****************************************************************

 THE SOLVENT EXTRACTION CONDITIONS ARE AS FOLLOWS:

     TEMPERATURE (IN DEGREES CENTIGRADE):  50
     CONTACT TIME (IN MINUTES): 3.0
     O/A RATIO:  1.00

 THE VOLUME FLOW RATE(L/D) OF ORGANIC SOLUTION REQUIRED IS:  161716.
     THE VOLUME % DEHPA IN THE ORGANIC SOLUTION IS:  40.00
     THE VOLUME % KERMAC 510 IN THE ORGANIC SOLUTION IS:  60.00
     THE VOLUME % O IN THE ORGANIC SOLUTION IS:  0.00
      198.0 SETS OF MIXING TANKS ARE REQUIRED, 4 STAGES PER SET.

*****************************************************************

THE  PH FOR STAGE  1 IS  1.20

THE EXTRACTION EFFICIENCYS FOR STAGE  1 ARE:
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     F
  0.00   0.00  35.00  35.00   0.00  18.80   0.00  80.00  23.00   0.00   0.00   0.00
*****************************************************************

THE AQUEOUS EXITING STAGE  1 CONTAINS (G/L):
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     F
  0.02   3.22   0.00   2.11   2.86   0.08   0.70   0.03   0.58   0.00   0.00   0.50
*****************************************************************

THE ORGANIC EXITING STAGE  1 CONTAINS (G/L):
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     F
  0.01   0.00   0.00   3.19   0.00   0.08   0.00   0.14   0.61   0.00   0.00   0.00
*******************************************************


*****************************************************************

THE  PH FOR STAGE  2 IS  2.00

THE EXTRACTION EFFICIENCYS FOR STAGE  2 ARE:
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
 50.00   0.00  88.00  88.00   0.00   0.00   0.00  82.00  59.00   0.00   0.00   0.00
*****************************************************************

THE AQUEOUS EXITING STAGE  2 CONTAINS (G/L):
    CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.01   3.22   0.00   0.25   2.86   0.08   0.70   0.01   0.24   0.00   0.00   0.50
```

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TABLE 8.147. CONTINUED

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***************************************************************
 THE ORGANIC EXITING STAGE  2 CONTAINS (G/L):
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.01    0.00    0.00    2.05    0.00    0.06    0.00    0.03    0.44    0.00    0.00    0.00
******************************************************

***************************************************************
THE  PH FOR STAGE  3 IS  1.50

THE EXTRACTION EFFICIENCYS FOR STAGE  3 ARE:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
  30.00    0.00   65.00   65.00    0.00   46.70    0.00   55.00   28.00    0.00    0.00    0.00
***************************************************************
THE AQUEOUS EXITING STAGE  3 CONTAINS (G/L):
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.01    3.22    0.00    0.09    2.86    0.05    0.70    0.00    0.17    0.00    0.00    0.50
***************************************************************
THE ORGANIC EXITING STAGE  3 CONTAINS (G/L):
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.00    0.00    0.00    0.19    0.00    0.06    0.00    0.00    0.10    0.00    0.00    0.00
******************************************************
***************************************************************
THE  PH FOR STAGE  4 IS  1.30

THE EXTRACTION EFFICIENCYS FOR STAGE  4 ARE:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.00    0.00   30.00   30.00    0.00   41.40    0.00   25.00   18.40    0.00    0.00    0.00
***************************************************************
THE AQUEOUS EXITING STAGE  4 CONTAINS (G/L):
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.01    3.22    0.00    0.06    2.86    0.03    0.70    0.00    0.14    0.00    0.00    0.50
***************************************************************
THE ORGANIC EXITING STAGE  4 CONTAINS (G/L):
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.00    0.00    0.00    0.03    0.00    0.02    0.00    0.00    0.03    0.00    0.00    0.00
******************************************************

***************************************************************
THE ORGANIC TO THE STRIPPING PROCESS CONTAINS:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.01    0.00    0.00    3.19    0.00    0.08    0.00    0.14    0.61    0.00    0.00    0.00
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TABLE 8.147. CONTINUED

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THE FINAL AQUEOUS SOLUTION CONTAINS:
   CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.01   3.22   0.00   0.06   2.86   0.03   0.70   0.00   0.14   0.00   0.00   0.50
*****************************************************************
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       GENERAL EXTRACTION PROGRAM :  CHROMIUM OXIDATION

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GPL IN STARTING SOLUTION:
   CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.01   3.22   0.00   0.06   2.86   0.03   0.70   0.00   0.14   0.00   0.00   0.50

THE LITERS/DAY STARTING SOLUTION:  161716.

THE PERCENT EXTRACTIONS:
   CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.0    0.0    0.0    0.0   14.7    0.0    0.0   95.0   42.8    0.0    0.0    0.0

 POUNDS METALS ENTERING PROCESS:
   CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  2.6 1148.9    0.0   22.1 1019.4    9.5  248.6    0.6   49.6    0.0    0.0  179.0
NEW GPL VALUES - SOLUTION EXITING PROCESS :
   CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.01   3.22   0.00   0.06   2.44   0.03   0.70   0.00   0.08   0.00   0.00   0.50


THE MOLE. WT. OF THE PRECIP. SPECIES:
   CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.0    0.0    0.0    0.0  103.0    0.0    0.0  107.0   78.0    0.0    0.0    0.0
THE MOLES OF PRECIP. SPECIES PRODUCED PER MOLE METAL:
   CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  1.0    1.0    1.0    1.0    1.0    1.0    1.0    1.0    1.0    1.0    1.0    1.0
THE PPD OF EACH PRECIP. SPECIES:
   CU     NI     CD     ZN     CR     CA     NA     FE     AL     PB     SI     P
  0.0    0.0    0.0    0.0  296.8    0.0    0.0    1.1   61.4    0.0    0.0    0.0
THE TOTAL PPD OF SOLID SPECIES PRECIP:  359.3

GPL ACID IN SOLN:  0.0
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TABLE 8.147. CONTINUED

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    GENERAL EXTRACTION PROGRAM :  LEAD CHROMATE PRECIPITATION.

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GPL IN STARTING SOLUTION:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
  0.01    3.22    0.00    0.06    2.44    0.03    0.70    0.00    0.08    0.00    0.00    0.50

THE LITERS/DAY STARTING SOLUTION:  161716.

THE PERCENT EXTRACTIONS:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.0     0.0     0.0     0.0    99.6     0.0     0.0     0.0   100.0     0.0     0.0     0.0


 POUNDS METALS ENTERING PROCESS:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   2.6  1148.9     0.0    22.1   869.6     9.5   248.6     0.0    28.4     0.0     0.0   179.0

NEW GPL VALUES - SOLUTION EXITING PROCESS :
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
  0.01    3.22    0.00    0.06    0.01    0.03    0.70    0.00    0.00    0.00    0.00    0.50


THE MOLE. WT. OF THE PRECIP. SPECIES:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.0     0.0     0.0     0.0   323.1     0.0     0.0     0.0     0.0     0.0     0.0     0.0

THE MOLES OF PRECIP. SPECIES PRODUCED PER MOLE METAL:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   1.0     1.0     1.0     1.0     1.0     1.0     1.0     1.0     1.0     1.0     1.0     1.0

THE PPD OF EACH PRECIP. SPECIES:
    CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.0     0.0     0.0     0.0  5380.3     0.0     0.0     0.0     0.0     0.0     0.0     0.0

THE TOTAL PPD OF SOLID SPECIES PRECIP:  5380.3

GPL ACID IN SOLN:  0.0


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    GENERAL EXTRACTION PROGRAM :  NICKEL SULFIDE PRECIPITATION.

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TABLE 8.147. CONTINUED

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GPL IN STARTING SOLUTION:
     CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.01    3.22    0.00    0.06    0.01    0.03    0.70    0.00    0.00    0.00    0.00   0.50

THE LITERS/DAY STARTING SOLUTION:  161716.

THE PERCENT EXTRACTIONS:
     CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   95.0    99.8    95.0    95.0    10.0     0.0     0.0    95.0     0.0    95.0     0.0 100.0

 POUNDS METALS ENTERING PROCESS:
     CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
    2.6  1148.9     0.0    22.1     3.5     9.5   248.6     0.0     0.0     0.0     0.0 179.0

NEW GPL VALUES - SOLUTION EXITING PROCESS :
     CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   0.00    0.01    0.00    0.00    0.01    0.03    0.70    0.00    0.00    0.00    0.00   0.00



THE MOLE. WT. OF THE PRECIP. SPECIES:
     CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
   96.0    91.0   144.0    97.0     0.0     0.0     0.0    88.0     0.0   239.0     0.0   95.0

THE MOLES OF PRECIP. SPECIES PRODUCED PER MOLE METAL:
     CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
    1.0     1.0     1.0     1.0     1.0     1.0     1.0     1.0     1.0     1.0     1.0    1.0

THE PFD OF EACH PRECIP. SPECIES:
     CU      NI      CD      ZN      CR      CA      NA      FE      AL      PB      SI      P
 [illegible].7  1777.3     0.0    31.2     0.0     0.0     0.0     0.0     0.0     0.0     0.0 548.8

THE TOTAL PFD OF SOLID SPECIES PRECIP:  2361.1

GPL ACID IN SOLN:  0.0
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